

PATENT COOPERATION TREATY

From the INTERNATIONAL BUREAU

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

To:

Commissioner
US Department of Commerce
United States Patent and Trademark
Office, PCT
2011 South Clark Place Room
CP2/5C24
Arlington, VA 22202
ETATS-UNIS D'AMERIQUE
in its capacity as elected Office

Date of mailing (day/month/year) 17 May 2001 (17.05.01)	
International application No. PCT/ZA00/00162	Applicant's or agent's file reference INT1009/MAJR
International filing date (day/month/year) 05 September 2000 (05.09.00)	Priority date (day/month/year) 07 September 1999 (07.09.99)
Applicant DEW, David, William et al	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
16 February 2001 (16.02.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer <p style="text-align: center;">R. Forax</p> Telephone No.: (41-22) 338.83.38
---	---

PCT

From the INTERNATIONAL SEARCHING AUTHORITY

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

To:

McCALLUM RADEMEYER & FREIMOND
P.O. Box 1130
7 Maclyn House, Bordeaux
2125 Randburg
SOUTH AFRICADate of mailing
(day/month/year)

12/12/2000

Applicant's or agent's file reference

INT1009/MAJR

FOR FURTHER ACTION

See paragraphs 1 and 4 below

International application No.

PCT/ZA 00/00162

International filing date
(day/month/year)

05/09/2000

Applicant

BILLITON INTELLECTUAL PROPERTY B.V. et al.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:
- ☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority



European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Maria Van der Hoeven

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

What documents must/may accompany the amendments?

Letter (Section 205(b)):

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged;
- (ii) the claim is cancelled;
- (iii) the claim is new;
- (iv) the claim replaces one or more claims as filed;
- (v) the claim is the result of the division of a claim as filed.

The following examples illustrate the manner in which amendments must be explained in the accompanying letter:

1. [Where originally there were 48 claims and after amendment of some claims there are 51]:
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers; claims 30, 33 and 36 unchanged; new claims 49 to 51 added."
2. [Where originally there were 15 claims and after amendment of all claims there are 11]:
"Claims 1 to 15 replaced by amended claims 1 to 11."
3. [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:
"Claims 1 to 6 and 14 unchanged; claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
4. [Where various kinds of amendments are made]:
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14; claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

"Statement under article 19(1)" (Rule 46.4)

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

It must be in the language in which the international application is to be published.

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

Consequence if a demand for international preliminary examination has already been filed

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

Consequence with regard to translation of the international application for entry into the national phase

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference INT1009/MAJR	FOR FURTHER ACTION see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. PCT/ZA 00/ 00162	International filing date (day/month/year) 05/09/2000	(Earliest) Priority Date (day/month/year) 07/09/1999
Applicant BILLITON INTELLECTUAL PROPERTY B.V. et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.



It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.



the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).

- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :



contained in the international application in written form.



filed together with the international application in computer readable form.



furnished subsequently to this Authority in written form.



furnished subsequently to this Authority in computer readable form.



the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.



the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the **title**,



the text is approved as submitted by the applicant.



the text has been established by this Authority to read as follows:

RECOVERY OF NICKEL FROM NICKEL BEARING SULPHIDE MINERALS BY BIOLEACHING

5. With regard to the **abstract**,



the text is approved as submitted by the applicant.



the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.



as suggested by the applicant.



because the applicant failed to suggest a figure.



because this figure better characterizes the invention.

5



None of the figures.

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C22B3/18 C22B23/00 B22F9/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C22B B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 225 256 A (TOLMIN MINERAL TECHNOLOGIES NV) 30 May 1990 (1990-05-30) page 1, line 15 -page 2, line 13; claims 1,3-6,8-13,20-23; figures 1-8 page 6, line 19 -page 7, line 20 ---	1-5, 7, 10-39
Y	US 5 007 620 A (EMMETT JR ROBERT C ET AL) 16 April 1991 (1991-04-16) column 15, line 49 - line 65; figures 1-7,20,21,33 column 19, line 3 - line 12 column 21, line 45 - line 53 ---	1-5, 7, 10-39
Y	WO 98 26100 A (BHP MINERALS INT INC) 18 June 1998 (1998-06-18) example 2 --- -/--	1-5, 7, 10-37

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

A document defining the general state of the art which is not considered to be of particular relevance

E earlier document but published on or after the international filing date

L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

O document referring to an oral disclosure, use, exhibition or other means

P document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

4 December 2000

Date of mailing of the international search report

12/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Bombeke, M

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 291 870 A (GENCOR LTD) 7 February 1996 (1996-02-07) page 4 -page 6 ----	1, 4, 5, 7, 19-21
Y	WO 99 09226 A (JONES DAVID L ;COMINCO ENG SERVICES (CA)) 25 February 1999 (1999-02-25) figures 2-4 ----	2-5, 7, 10, 39
Y	EP 0 808 910 A (UNIV MICHIGAN TECH) 26 November 1997 (1997-11-26) column 8, line 3 - line 25; figure 1 ----	38
P, X	WO 00 29629 A (MILLER PAUL CHARLES ;RHODES MIKE (AU); WINBY RICHARD (AU); BACTECH) 25 May 2000 (2000-05-25) page 3, line 14 -page 4, line 26 -----	1, 11, 16-34

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 2225256	A	30-05-1990	AU 630889 B	12-11-1992
			AU 4262989 A	12-04-1990
			US 5021069 A	04-06-1991
			ZA 8907627 A	25-09-1991
US 5007620	A	16-04-1991	US 4974816 A	04-12-1990
			US 4732608 A	22-03-1988
			AT 78240 T	15-08-1992
			AU 607901 B	21-03-1991
			AU 6858087 A	13-08-1987
			CA 1329989 A	07-06-1994
			DE 3780452 A	20-08-1992
			DE 3780452 D	20-08-1992
			DE 3780452 T	11-03-1993
			EP 0294387 A	14-12-1988
			ES 2001827 A	16-06-1988
			FI 883604 A	01-08-1988
			GR 870202 A	05-06-1987
			JP 63502796 T	20-10-1988
			NZ 219219 A	26-04-1990
			WO 8704694 A	13-08-1987
			US 5057284 A	15-10-1991
			US 5227136 A	13-07-1993
			ZW 15687 A	28-10-1987
			BR 8700558 A	08-12-1987
			US 4968008 A	06-11-1990
			US 4728082 A	01-03-1988
			ZA 8606691 A	24-06-1987
			ZA 8700817 A	28-10-1987
			ZM 1587 A	28-03-1988
			ZW 11686 A	18-02-1987
WO 9826100	A	18-06-1998	US 5626648 A	06-05-1997
			AU 720713 B	08-06-2000
			AU 1288697 A	03-07-1998
			BR 9612802 A	28-03-2000
			EP 0948655 A	13-10-1999
GB 2291870	A	07-02-1996	AU 689598 B	02-04-1998
			AU 2726295 A	15-02-1996
			CA 2155051 A	02-02-1996
			FI 953487 A	02-02-1996
			ZA 9506204 A	12-03-1996
WO 9909226	A	25-02-1999	AU 8796398 A	08-03-1999
			AU 8847598 A	08-03-1999
			BR 9811945 A	22-08-2000
			WO 9909225 A	25-02-1999
			CN 1267338 T	20-09-2000
			CN 1271392 T	25-10-2000
			EP 1012351 A	28-06-2000
			EP 1012352 A	28-06-2000
			NO 20000727 A	21-03-2000
EP 0808910	A	26-11-1997	US 5827701 A	27-10-1998
			AU 725634 B	19-10-2000
			AU 2141197 A	27-11-1997
			CA 2205151 A	21-11-1997

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0808910 A		JP 10113694 A	06-05-1998
		US 6043022 A	28-03-2000
		ZA 9704368 A	24-08-1998
WO 0029629 A	25-05-2000	AU 1141400 A	05-06-2000

From the
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

McCALLUM RADEMEYER & FREIMOND
P.O. Box 1130
7 June Avenue, Bordeaux
2125 Randburg
AFRIQUE DU SUD

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL PRELIMINARY
EXAMINATION REPORT
(PCT Rule 71.1)

Date of mailing
(day/month/year) 21.12.2001

Applicant's or agent's file reference
INT1009/MAJR

IMPORTANT NOTIFICATION

International application No.
PCT/ZA00/00162

International filing date (day/month/year)
05/09/2000

Priority date (day/month/year)
07/09/1999

Applicant
BILLITON INTELLECTUAL PROPERTY B.V. et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.


4. REMINDER

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA/

 European Patent Office - P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk - Pays Bas
Tel. +31 70 340 - 2040 Tx: 31 651 epo nl
Fax: +31 70 340 - 3016

Authorized officer

Dekker, M

Tel.+31 70 340-4046



PCT

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference INT1009/MAJR	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/ZA00/00162	International filing date (day/month/year) 05/09/2000	Priority date (day/month/year) 07/09/1999
International Patent Classification (IPC) or national classification and IPC C22B3/18		
Applicant BILLITON INTELLECTUAL PROPERTY B.V. et al.		



1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.

☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 5 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☐ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 16/02/2001	Date of completion of this report 21.12.2001
Name and mailing address of the international preliminary examining authority:  European Patent Office - P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk - Pays Bas Tel. +31 70 340 - 2040 Tx: 31 651 epo nl Fax: +31 70 340 - 3016	Authorized officer Bombeke, M Telephone No. +31 70 340 3576 

INTERNATIONAL PRELIMINARY EXAMINATION REPORT

International application No. PCT/ZA00/00162

I. Basis of the report

1. With regard to the **elements** of the international application (*Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17)*):

Description, pages:

1-25 as originally filed

Claims, No.:

1-26 filed with the demand

Drawings, sheets:

1/5-5/5 as originally filed

2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.

These elements were available or furnished to this Authority in the following language: , which is:

- ☐ the language of a translation furnished for the purposes of the international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of a translation furnished for the purposes of international preliminary examination (under Rule 55.2 and/or 55.3).

3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:

- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished.

4. The amendments have resulted in the cancellation of:

- ☐ the description, pages:
- ☐ the claims, Nos.:

**INTERNATIONAL PRELIMINARY
EXAMINATION REPORT**

International application No. PCT/ZA00/00162

☐ the drawings, sheets:

5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

(Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report.)

6. Additional observations, if necessary:

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	1-26
	No:	Claims	
Inventive step (IS)	Yes:	Claims	1-26
	No:	Claims	
Industrial applicability (IA)	Yes:	Claims	1-26
	No:	Claims	

2. Citations and explanations
see separate sheet

VIII. Certain observations on the international application

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:
see separate sheet

Re Item V

Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

The subject-matter of claims 1-24 resp. 25,26 to a method resp. a plant for recovering nickel from a sulphide mineral slurry by bioleaching is novel and inventive vis-à-vis the cited prior art, in particular document US-A-5007620, because said prior art does not disclose nor fairly suggests the provision of the claimed control feature which involves controlling the dissolved oxygen concentration in the bioleach slurry at a particular level by controlling (in response to the measured oxygen concentration) the feed gas supply to the bioreactor.

It follows that claims 1-26 meet the requirements of Articles 33(2) and 33(3) PCT.

Re Item VIII

Certain observations on the international application

Claims 1 and 25 do not meet the requirements of Article 6 PCT in that the matter for which protection is sought is not clearly defined. The following functional statements do not enable the skilled person to determine which concrete technical measures are necessary to perform the stated functions:

- claim 1: "controlling" the dissolved oxygen concentration by "controlling" at least one of the following ...

- claim 24: "control mechanism" whereby, in response to ... the supply of oxygen

Moreover the control measures mentioned in claim 1 are not consistent with the control means defined in claim 25.

Furthermore the reactor part of claim 25 does not contain all the features essential to its definition and functioning (Article 6 and Rule 6(3)b PCT), nor is it clear how the bio-reactor is operatively connected with the undefined nickel recovery system (figures 1 and 5).

CLAIMS

1. A method of recovering nickel from a nickel bearing sulphide mineral slurry which includes the steps of:
 - (a) subjecting the slurry in a reactor to a bioleaching process at a temperature in excess of 40°C;
 - (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry;
 - (c) controlling the dissolved oxygen concentration in the slurry at a level of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$ by controlling at least one of the following: the oxygen content of the feed gas; the feed gas supply rate; the rate of feed of the slurry to the reactor; and
 - (d) recovering nickel from a bioleach residue of the bioleaching process.
2. A method according to claim 1 wherein copper is removed from the bioleach residue before recovering nickel therefrom.
3. A method according to claim 2 wherein cobalt is removed from the bioleach residue before recovering nickel therefrom.
4. A method according to any one of claims 1 to 3 which includes the step of removing iron from the bioleach residue before recovering nickel therefrom.
5. A method according to claim 4 wherein the iron is precipitated from the bioleach residue by the addition of limestone to the residue.
6. A method according to claim 5 wherein carbon dioxide generated in the iron precipitation step is fed to the feed gas of step (b) or directly to the slurry.

7. A method according to any one of claims 1 to 6 wherein, in step (d), nickel is recovered using a solvent extraction and electrowinning process.
8. A method according to claim 7 wherein oxygen generated during the nickel electrowinning is fed to the feed gas of step (b) or directly to the slurry.
9. A method according to any one of claims 1 to 6 wherein, in step (d), nickel is recovered using a pressure hydrogen reduction process and nitrogen, produced during the generation of the feed gas supplied to the slurry in step (b), is used for purging autoclaves used for nickel powder production in the pressure hydrogen reduction process.
10. A method according to any one of claims 1 to 9 which is operated in parallel to a process for recovering nickel from lateritic ores by pressure acid leaching to produce a nickel laterite ore slurry and which includes the step of adding the bioleach residue to the nickel laterite residue slurry before carrying out step (d).
11. A method according to any one of claims 1 to 10 wherein the feed gas contains in excess of 85% oxygen by volume.
12. A method according to any one of claims 1 to 11 which includes the step of controlling the carbon content of the slurry.
13. A method according to any one of claims 1 to 12 which includes the step of controlling the carbon dioxide content of the slurry in the range of from 0.5% to 5.0% by volume.
14. A method according to any one of claims 1 to 13 wherein the bioleaching process is carried out at a temperature in the range of from 40°C to 100°C.

15. A method according to claim 14 wherein the said temperature is in the range of from 60°C to 85°C.
16. A method according to any one of claims 1 to 13 which includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms.
17. A method according to claim 16 wherein the microorganisms are selected from the following genus groups: *Acidithiobacillus*; *Thiobacillus*; *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.
18. A method according to claim 16 or 17 wherein the said microorganisms are selected from the following species: *Acidithiobacillus caldus* (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*); *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus acidophilus*); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.
19. A method according to any one of claims 1 to 14 which includes the step of bioleaching the slurry at a temperature of from 45°C to 60°C using moderate thermophile microorganisms.
20. A method according to claim 19 wherein the microorganisms are selected from the following genus groups: *Acidithiobacillus* (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma* (*Ferriplasma*); and *Alicyclobacillus*.
21. A method according to claim 19 or 20 wherein the said microorganisms are selected from the following species: *Acidithiobacillus caldus* (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus*

disulfidooxidans; Sulfobacillus thermosulfidooxidans; Ferroplasma acidarmanus; Thermoplasma acidophilum; and Alicyclobacillus acidocaldrius.

22. A method according to claim 15 which includes the step of bioleaching the slurry at a temperature of from 60°C to 85°C using thermophilic microorganisms.
23. A method according to claim 22 wherein the microorganisms are selected from the following genus groups: *Acidotherrnus; Sulfolobus; Metallosphaera; Acidianus; Ferroplasma (Ferriplasma); Thermoplasma; and Picrophilus.*
24. A method according to claim 22 or 23 wherein the said microorganisms are selected from the following species: *Sulfolobus metallicus; Sulfolobus acidocaldarius; Sulfolobus thermosulfidooxidans; Acidianus infernus; Metallosphaera sedula; Ferroplasma acidarmanus; Thermoplasma acidophilum; Thermoplasma volcanium; and Picrophilus oshimae.*
25. A plant for recovering nickel from a nickel bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a nickel bearing sulphide mineral slurry to the vessel wherein a bioleaching process is carried out at a temperature in excess of 40°C, an oxygen source which supplies oxygen in the form of oxygen enriched air or substantially pure oxygen to the slurry, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measured dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$, and a recovery system which recovers nickel from a bioleach residue from the reactor vessel.
26. A plant according to claim 25 which includes an installation for recovering nickel from lateritic ores by pressure acid leaching to produce a nickel laterite residue slurry

which is combined with the said bioleach residue from the reactor vessel, and the combined slurry and residue are fed to the said recovery system.



(43) International Publication Date
15 March 2001 (15.03.2001)

PCT

(10) International Publication Number
WO 01/18268 A1

(51) International Patent Classification: C22B 3/18.
23/00, B22F 9/26

Johannesburg (ZA). CRUNDWELL, Frank [ZA/ZA];
200 Hans Strijdom Drive, 2194 Randburg (ZA).

(21) International Application Number: PCT/ZA00/00162

(74) Agent: RADEMEYER, Montague, Ampie, John; Mc-
Callum Rademeyer & Freimond, P.O. Box 1130, 7 Maclyn
House, 2125 Bordeaux (ZA).

(22) International Filing Date:
5 September 2000 (05.09.2000)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
99/5746 7 September 1999 (07.09.1999) ZA

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ,
DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR,
HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR,
LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ,
NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM,
TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian
patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European
patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE,
IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG,
CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

Published:

(75) Inventors/Applicants (*for US only*): DEW, David,
William [ZA/ZA]; 33 Alphen Close, Wroxham Road,
Paulshof, 2196 Sandton (ZA). BASSON, Petrus [ZA/ZA];
10 Lourie's Loft, Perm Street, Sonneglans, 2194 Randburg
(ZA). NORTON, Alan [ZA/ZA]; 6 Hollard Street, 2001

— With international search report.

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: RECOVERY OF NICKEL FROM NICKEL BEARING SULPHIDE MINERALS BY BIOLEACHING

(57) Abstract: A method of recovering nickel from a nickel bearing sulphide mineral slurry which includes the steps of subjecting the slurry to a bioleaching process, supplying a feed gas which contains in excess of 21 % oxygen by volume, to the slurry, and recovering nickel from a bioleach residue of the bioleaching process.

WO 01/18268 A1



BACKGROUND OF THE INVENTION

5 This invention relates to the recovery of nickel from nickel bearing sulphide minerals.

Commercial bioleach plants which are currently in operation treating sulphide minerals, typically operate within the temperature range of 40°C to 50°C and rely on sparging air to the bioleach reactors to provide the required oxygen. Operation at this relatively low temperature and the use of air to supply oxygen, limit the rate of sulphide mineral oxidation that can be achieved.

The use of high temperatures between 50°C and 100°C greatly increases the rate of sulphide mineral leaching.

15 The solubility of oxygen is however limited at high temperatures and the rate of sulphide mineral leaching becomes limited. In the case of using air for the supply of oxygen, the effect of limited oxygen solubility is such that the rate of sulphide mineral leaching becomes dependent on and is limited by the rate of oxygen transfer from the gas to the liquid phase ^(1,2).

20 The bioleaching of nickel sulphide bearing minerals is similarly problematic and to the applicant's knowledge no commercial nickel bioleaching plants are in operation.

SUMMARY OF THE INVENTION

5 According to one aspect of the invention there is provided a method of recovering nickel from a nickel bearing sulphide mineral slurry which includes the steps of:

- (a) subjecting the slurry to a bioleaching process,
- (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry, and
- 25 (c) recovering nickel from a bioleach residue of the bioleaching process.

If the slurry contains copper then preferably copper is removed from the bioleach residue before recovering nickel therefrom.

5 The method may include the step of recovering cobalt from the bioleach residue before recovering nickel therefrom.

10 Iron may also be removed from the bioleach residue before recovering nickel therefrom. The iron may be precipitated from the bioleach residue by the addition of limestone to the residue, or in any other suitable way. Carbon dioxide generated in the iron precipitation step may be fed to the feed gas of step (b) or directly to the slurry.

15 In step (c) nickel may be recovered using any appropriate technique. Use may for example be made of a solvent extraction and electrowinning process. In this instance oxygen generated during the nickel electrowinning step may be fed to the feed gas of step (b) or directly to the slurry.

It is also possible to recover nickel, in step (c), using a pressure hydrogen reduction process. In this case nitrogen, produced during the generation of the feed gas which is supplied to the slurry in step (b), may be used for purging autoclaves used for nickel powder production in the pressure hydrogen reduction process.

20 The introduction of pressure acid leaching (PAL) for the recovery of nickel from lateritic ores opens up additional opportunities for bioleaching of nickel bearing sulphides. The volumes arising down stream of PAL processes are roughly an order of magnitude higher than the mass of nickel sulphide concentrates arising from sulphide nickel mines (approximately 1- 3 million tonnes per annum versus approximately 20-200 thousand tonnes per annum).

5 Since residues from both processes are similar in nature (low pH, solubilised nickel and iron) it is advantageous to treat the bioleach residue for nickel and cobalt recovery using the larger PAL downstream process equipment. Thus feeding a nickel sulphide bioleach residue slurry into a PAL residue slurry and

treating both streams together hereafter would bring about considerable economies of scale in terms of capital and operating costs.

Thus the invention also extends to operating the aforementioned method in parallel to a process for recovering nickel from lateritic ores by pressure acid leaching to produce a nickel laterite residue slurry and then adding the bioleach residue to the nickel laterite ore slurry before carrying out step (c).

As used herein the expression "oxygen enriched gas" is intended to include a gas, e.g. air, which contains in excess of 21% oxygen by volume. This is an oxygen content greater than the oxygen content of air. The expression "pure oxygen" is intended to include a gas which contains in excess of 85% oxygen by volume.

Preferably the feed gas which is supplied to the slurry contains in excess of 85% oxygen by volume i.e. is substantially pure oxygen.

The method may include the step of maintaining the dissolved oxygen concentration in the slurry within a desired range which may be determined by the operating conditions and the type of microorganisms used for leaching. The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation, is in the range of from 0.2×10^{-3} kg/m³ to 4.0×10^{-3} kg/m³. On the other hand if the dissolved oxygen concentration is too high then microorganism growth is inhibited. The upper threshold concentration also depends on the genus and strain of microorganism used in the leaching process and typically is in the range of from 4×10^{-3} kg/m³ to 10×10^{-3} kg/m³.

Thus, preferably, the dissolved oxygen concentration in the slurry is maintained in the range of from 0.2×10^{-3} kg/m³ to 10×10^{-3} kg/m³.

The method may include the steps of determining the dissolved oxygen concentration in the slurry and, in response thereto, of controlling at least one of the following: the oxygen content of the feed gas, the rate of supply of the feed gas to the slurry, and the rate of feed of slurry to a reactor.

The dissolved oxygen concentration in the slurry may be determined in any appropriate way, e.g. by one or more of the following: by direct measurement of the dissolved oxygen concentration in the slurry, by measurement of the oxygen content in gas above the slurry, and indirectly by measurement of the oxygen content in off-gas from the slurry, taking into account the rate of oxygen supply, whether in gas enriched or pure form, to the slurry, and other relevant factors.

The method may include the step of controlling the carbon content of the slurry. This may be achieved by one or more of the following: the addition of carbon dioxide gas to the slurry, and the addition of other carbonaceous material to the slurry.

The method may extend to the step of controlling the carbon dioxide content of the feed gas to the slurry in the range of from 0.5% to 5% by volume. A suitable figure is of the order of 1% to 1.5% by volume. The level of the carbon dioxide is chosen to maintain high rates of microorganism growth and sulphide mineral oxidation.

The bioleaching process is preferably carried out at an elevated temperature. As stated hereinbefore the bioleaching rate increases with an increase in operating temperature. Clearly the microorganisms which are used for bioleaching are determined by the operating temperature and vice versa. As the addition of oxygen enriched gas or substantially pure oxygen to the slurry has a cost factor it is desirable to operate at a temperature which increases the leaching rate by an amount which more than compensates for the increase in operating cost. Thus, preferably, the bioleaching is carried out at a temperature in excess of 40°C.

The bioleaching may be carried out at a temperature of up to 100°C or more and preferably is carried out at a temperature which lies in a range of from 60°C to 85°C.

In one form of the invention the method includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms. These microorganisms may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

In order to operate at this temperature the said microorganisms may, for example, be selected from the following species:

Acidithiobacillus caldus (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*);
Acidithiobacillus ferrooxidans (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus*
5 *acidophilus*); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and
Acidiphilium cryptum.

If the bioleaching step is carried out at a temperature of from 45°C to 60°C then moderate thermophile microorganisms may be used. These may, for example, be selected from the following genus groups:

1) *Acidithiobacillus* (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma* (*Ferriplasma*); and
Alicyclobacillus.

Suitable moderate thermophile microorganisms may, for example, be selected from the following species:

Acidithiobacillus caldus (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus*
15 *acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*;
Thermoplasma acidophilum; and *Alicyclobacillus acidocaldrius*.

It is preferred to operate the leaching process at a temperature in the range of from 60°C to 85°C using thermophilic microorganisms. These may, for example, be selected from the following genus groups:

2) *Acidothermus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma* (*Ferriplasma*); *Thermoplasma*; and
Picrophilus.

Suitable thermophilic microorganisms may, for example, be selected from the following species:

Sulfolobus metallicus; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*;
5 *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*;
and *Picrophilus oshimae*.

The slurry may be leached in a reactor tank or vessel which is open to atmosphere or substantially closed. In the latter case vents for off-gas may be provided from the reactor.

According to a different aspect of the invention there is provided a method of recovering nickel from a slurry containing nickel bearing sulphide minerals which includes the steps of bioleaching the slurry using a suitable microorganism at a temperature in excess of 40°C, controlling the dissolved oxygen concentration in the slurry within a predetermined range, and recovering nickel from a bioleach residue.

5

The said dissolved oxygen concentration may be controlled by controlling the supply of oxygen to the slurry.

The oxygen may be supplied to the slurry in the form of oxygen enriched gas or substantially pure oxygen.

10

The said operating temperature is preferably above 60°C and may be in the range of 60°C to 85°C.

The invention also extends to a method of enhancing the oxygen mass transfer coefficient from a gas phase to a liquid phase in a nickel bearing sulphide mineral slurry which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume to the slurry.

15

The feed gas preferably contains in excess of 85% oxygen by volume.

The invention further extends to a method of bioleaching an aqueous slurry containing nickel bearing sulphide minerals which includes the steps of bioleaching the slurry at a temperature above 60°C and supplying gas containing in excess of 21% oxygen by volume to the slurry to maintain the dissolved oxygen concentration in the slurry in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

20

The invention is also intended to cover a plant for recovering nickel from a nickel bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a nickel bearing sulphide mineral slurry to the vessel, an oxygen source, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measure of dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry within a predetermined range, and a recovery system which recovers nickel from a bioleach residue from the reactor vessel.

25

The plant may include an installation for recovering nickel from lateritic ores by pressure acid leaching to produce a nickel laterite residue slurry which is combined with the said bioleach residue from the reactor, and the combined slurry and residue are fed to the said recovery system.

5

Various techniques may be used for controlling the supply of oxygen to the slurry and hence for controlling the dissolved oxygen concentration in the slurry at a desired value. Use may for example be made of valves which are operated manually. For more accurate control use may be made of an automatic control system. These techniques are known in the art and are not further described herein.

As has been indicated oxygen and carbon dioxide may be added to the slurry in accordance with predetermined criteria. Although the addition of these materials may be based on expected demand and measurement of other performance parameters, such as iron(II) concentration, it is preferred, however, to make use of suitable measurement probes to sample the actual values of the critical parameters.

5

For example use may be made of a dissolved oxygen probe to measure the dissolved oxygen concentration in the slurry directly. To achieve this the probe is immersed in the slurry. The dissolved oxygen concentration may be measured indirectly by using a probe in the reactor off-gas or by transmitting a sample of the off-gas, at regular intervals, to an oxygen gas analyser. Again it is pointed out that measuring techniques of this type are known in the art and accordingly any appropriate technique can be used.

7

A preferred approach to the control aspect is to utilise one or more probes to measure the dissolved oxygen concentration in the slurry, whether directly or indirectly. The probes produce one or more control signals which are used to control the operation of a suitable valve or valves, e.g. solenoid valves, automatically so that the supply of oxygen to an air stream which is being fed to the slurry is varied automatically in accordance with real time measurements of the dissolved oxygen concentration in the slurry

5

Although it is preferred to control the addition of oxygen to a gas stream which is fed to the slurry a reverse approach may be adopted in that the oxygen supply rate to the reactor vessel may be maintained

substantially constant and the rate of supply of the sulphide mineral slurry to the reactor vessel may be varied to achieve a desired dissolved oxygen concentration.

The invention is not limited to the actual control technique employed and is intended to extend to variations of the foregoing approaches and to any equivalent process.

Nickel bearing sulphide flotation concentrates frequently contain violarite and pyrrhotite and the method of the invention is of particular benefit, because both pyrrhotite and violarite have a high leaching rate, even at typical mesophile operating temperatures, which is further increased at the higher temperatures used with moderate and extreme thermophiles. Thus the benefits of the invention, including a high specific reactor sulphide oxidation duty and reduced specific power requirement for oxidation, will be obtained during the bioleaching of nickel bearing sulphide concentrates, even at mesophile operating temperatures.

Nickel may be recovered from solution by any appropriate process, for example by solvent extraction applied to the solution or by resin-in-pulp applied to the slurry, followed by electrowinning. The route adopted by Anaconda Nickel for treatment of leach liquors arising from nickel laterites at Murrin Murrin is also relevant i.e. by precipitation of a sulphide (using hydrogen sulphide) and refining of the sulphide precipitate by re-leaching, purification and hydrogen reduction⁽⁷⁾. The route adopted by Preston Resources on a similar solution to that produced at Murrin Murrin at the Cawse project is also applicable, by precipitating a hydroxide (with magnesia), re-leaching, purification using solvent extraction and then electrowinning⁽⁷⁾. Lastly the same process used at Cawse but with the production of a nickel carbonate from the solvent extraction strip liquor, would be most suitable for the production of nickel rondelles by methods established by Queensland Nickel Limited.

If electrowinning is selected as the production method for nickel, the oxygen generated at the anode in the electrowinning process may be used to supplement that used in the bioleach process, reducing the capital and operating costs required for oxygen production.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further described by way of example with reference to the accompanying drawings in which:

Figure 1 is a schematic representation of a portion of a plant in which the invention is carried out,

5 Figures 2, 3 and 4 reflect various results and parameters obtained from operating a bioreactor using the principles of the invention, and

Figure 5 is a process flow sheet illustrating the recovery of nickel according to the invention, and various possible modifications.

10 DESCRIPTION OF PREFERRED EMBODIMENT

General Principles

The limitation of low oxygen solubility during bioleaching, using air, at high temperatures, which in turn limits
15 the rate of reaction, requires enrichment of the air with oxygen i.e. air with an oxygen content greater than 21% by volume, or the use of pure oxygen (defined as being greater than 85% oxygen by volume). The use of oxygen enriched air or pure oxygen overcomes the limited rate of reaction due to oxygen supply constraints, but has two major disadvantages:

- a) the provision of oxygen enriched air or pure oxygen is expensive and requires a high utilisation (>60%) of
20 the oxygen to warrant the additional expense ⁽³⁾; and
- b) if the oxygen level in solution becomes too high microorganism growth is prevented and sulphide mineral bioleaching stops ⁽⁴⁾.

Therefore, in order to realise the benefits of high rates of sulphide mineral leaching at high temperatures in
25 commercial bioleaching plants, the drawbacks of requiring expensive oxygen and the risk of failure if the dissolved oxygen levels become too high must be overcome.

The bioleaching of sulphide minerals at an elevated temperature results in a high rate of sulphide mineral oxidation, but is dependent on the supply of oxygen and carbon dioxide to maintain high rates of sulphide

mineral oxidation and of microorganism growth at adequate rates. The absorption of oxygen and carbon dioxide in the bioleaching reactor is limited, in each case, by the rate of mass transfer from the gas phase into the solution phase. For oxygen the rate of oxygen absorption is defined by equation (1) as follows:

$$R = M \cdot (C^* - C_L) \quad (1)$$

where:

R = Oxygen demand as mass (kg) per unit volume (m^3) per unit time(s) ($kg/m^3/s$),

M = Oxygen mass transfer coefficient in reciprocal seconds (s^{-1}),

C^* = Saturated dissolved oxygen concentration as mass (kg) per unit volume (m^3) (kg/m^3),
and

C_L = Dissolved oxygen concentration in solution as mass (kg) per unit volume (m^3) (kg/m^3).

The factor $(C^* - C_L)$ is referred to as the oxygen driving force. A similar equation may be used to describe the rate of carbon dioxide supply to the solution. If the sulphide mineral oxidation rate is increased the oxygen demand increases proportionately. To meet a higher oxygen demand either the oxygen mass transfer coefficient (M) or the oxygen driving force $(C^* - C_L)$ must be increased.

An increase in the oxygen mass transfer coefficient may be achieved by increasing the power input to the bioleach reactor mixer. This improves gas dispersion in the sulphide mineral slurry. With this approach, however, an increase in the oxygen mass transfer coefficient of, for example, 40% requires an increase in the power input to the mixer by a factor of as much as 200%, with a commensurate increase in operating costs.

The oxygen driving force may be increased by increasing the saturated dissolved oxygen concentration C^* and reducing the dissolved oxygen concentration C_L .

Microorganism population growth is limited or prevented if the dissolved oxygen concentration C^* reaches too high a level. A concentration level above $4 \times 10^{-3} \text{ kg/m}^3$ has been found to be detrimental to *Sulfolobus*-like strains. Certain *Acidithiobacillus* strains, however, have been found to be tolerant to dissolved oxygen concentrations of up to $10 \times 10^{-3} \text{ kg/m}^3$.

The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. Thus, in order to provide an adequate, or optimum, supply of oxygen, the dissolved oxygen concentration in the sulphide mineral slurry must be monitored and, where appropriate, the addition of oxygen to the sulphide mineral slurry must be controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$.

On the other hand the dissolved oxygen concentration must not exceed an upper threshold value at which microorganism growth is prevented. It is pointed out that the upper threshold concentration depends on the genus and strain of microorganism used in the bioleaching process. A typical upper threshold value is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

As has been previously indicated the rate of sulphide mineral oxidation, which can be achieved when operating at a relatively low temperature of the order of from 40°C to 55°C , is limited. In order to increase the rate of oxidation it is desirable to make use of thermophiles and to operate at temperatures in excess of 60°C . Any suitable microorganism capable of operating within this temperature range may be used. The optimum operating temperature is dependent on the genus and type of microorganism used. Thus moderate thermophiles of the type *Sulfobacillus* are suitable for operating at a temperature of up to 65°C . Thermophiles of the type *Sulfolobus* are suitable for operating at temperatures of from 60°C to at least 85°C . *Sulfolobus metallicus*, for example, shows optimal growth in the temperature range of from 65°C to 70°C .

The applicant has established that the operation of the bioleaching process, using a gas enriched with oxygen, or pure oxygen, as the oxidant, at elevated temperatures of from 40°C to 85°C :

increases the specific sulphide oxidation duty of the reactor considerably;

results in an unexpected and significantly enhanced oxygen mass transfer rate;

increases the oxygen utilisation, providing that the dissolved oxygen concentration is controlled above the point where microorganism growth and mineral oxidation are prevented and below the point at which microorganism growth is inhibited; and

the overall power required for the oxidation of sulphide minerals is significantly reduced.

The method of the invention represents a significant improvement compared to a bioleach operation carried out at a temperature of from 40°C to 45°C with air.

The controlled addition of oxygen enriched air or pure oxygen directly into the bioreactor improves the oxygen utilisation efficiency. The oxygen utilisation for a conventional commercial bioleach plant (at least 100m³ in volume) operating at from 40°C to 45°C with air may be expected to achieve a maximum oxygen utilisation factor of from 40% to 50%. Consequently only 40% to 50% of the total mass of oxygen supplied to the bioleach plant is used to oxidise the sulphide minerals. With the method of the invention the oxygen utilisation is significantly higher, of the order of from 60% to 95%. The higher oxygen utilisation is achieved by controlled oxygen addition and results from the enhanced oxygen mass transfer rate and by operating at low dissolved oxygen concentrations in the solution phase.

It will be appreciated that although high oxygen demand in bioleach reactors has come about primarily by the use of higher temperatures, rapidly leaching sulphide minerals at temperatures below 60°C, using mesophile or moderate thermophile microorganisms, will have similarly high oxygen demands. The method of the invention is therefore not restricted to suit thermophiles or extreme thermophiles, but also mesophile and moderate thermophile microorganisms.

Another advantage of using air enriched with oxygen or pure oxygen is that the evaporation losses are reduced, because there is less inert gas removing water vapour from the top of the reactor. This is particularly important in areas where water is scarce or expensive.

In carrying out the method of the invention the temperature of the slurry in the bioleach vessel or reactor may be controlled in any suitable way known in the art. In one example the bioleach reactor is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry is regulated using any suitable cooling system, for example an internal cooling system.

Table 1 shows typical data for specific sulphide oxidation duty and oxygen utilisation, when bioleaching with air at 40°C to 45°C, in two commercial bioreactors, Plant A and Plant B respectively, (greater than 100m³ in volume).

Table 1 Commercial Bioreactor Performance Results

Description	Units	Plant A	Plant B
Reactor temperature	°C	42	40
Reactor operating volume	m ³	471	896
Oxygen utilisation	%	37.9	43.6
Typical dissolved oxygen concentration	mg/l	2.5	2.7
Oxygen mass transfer coefficient	s ⁻¹	0.047	0.031
Specific oxygen demand	kg/m ³ /day	21.6	14.8
Specific sulphide oxidation duty	kg/m ³ /day	8.9	5.7
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.8

At low temperatures (40°C – 50°C), with air as the inlet gas, which applies to the results for the commercial reactors, Plant A and Plant B, presented in Table 1, the oxygen utilisations achieved are expected and the oxygen mass transfer coefficients (M) correspond to the applicant's design value. The applicant has determined that if the method of the invention were to be applied to Plant A, the plant performance would be significantly increased, as indicated by the results presented in Table 2.

Table 2 Predicted Improvement in Commercial Bioreactor Performance

	Units	Plant A - typical operation	Plant A - using the method of the invention
Reactor temperature	°C	42	77
Microbial type strain	-	<i>Acidithiobacillus</i>	<i>Sulfolobus</i>
Inlet gas oxygen content	% by volume	20.9	90.0
Oxygen utilisation	%	37.9	93.0
Typical dissolved oxygen concentration	mg/l	2.5	2.5
Specific oxygen demand	kg/m ³ /day	21.6	59.5
Specific sulphide oxidation duty	kg/m ³ /day	8.9	24.5
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.2

The results clearly show the benefit of the invention in achieving higher rates of reaction by the combination of bioleaching at high temperature, adding oxygen enriched gas and by controlling the dissolved oxygen concentration to a predetermined low level (e.g. 0.2×10^{-3} kg/m³ to 4.0×10^{-3} kg/m³). The specific sulphide oxidation duty of the reactor is increased by almost threefold. Clearly the upper dissolved oxygen concentration should not be increased above a value at which microorganism growth is inhibited or stopped.

Even though additional capital for the production of oxygen is required, the savings in reactor and other costs at least offset this additional expense. Additionally, the specific power consumption per kg sulphide oxidised is decreased by approximately one-third. In a plant oxidising 300 tonnes of sulphide per day, the power saving, assuming a power cost of US\$0.05 per kWh, would amount to US\$2.8 million per annum. The high oxygen utilisation and increased specific sulphide oxidation capacity of the reactor represent in combination a considerable improvement over conventional bioleaching practice conducted at lower temperatures, with oxygen supplied by air.

Figure 1 of the accompanying drawings illustrates a non-limiting example of the invention and shows a bioleaching plant 10 in which bioleaching is carried out, in accordance with the principles of the invention.

5

The plant 10 includes a bioreactor 12 with an agitator or mixer 14 which is driven by means of a motor and gearbox assembly 16.

In use a tank or vessel 18 of the reactor contains a sulphide mineral slurry 20. An impeller 22 of the agitator is immersed in the slurry and is used for mixing the slurry in a manner which is known in the art.

A probe 24 is immersed in the slurry and is used for measuring the dissolved oxygen concentration in the slurry. A second probe 26, inside the tank 18 above the surface level 28 of the slurry, is used for measuring the carbon dioxide content in the gas 30 above the slurry 20.

15

An oxygen source 32, a carbon dioxide source 34 and an air source 36 are connected through respective control valves 38, 40 and 42 to a sparging system 44, positioned in a lower zone inside the tank 18, immersed in the slurry 20.

The probe 24 is used to monitor the dissolved oxygen concentration in the sulphide mineral slurry 20 and provides a control signal to a control device 46. The control device controls the operation of the oxygen supply valve 38 in a manner which is known in the art but in accordance with the principles which are described herein in order to maintain a desired dissolved oxygen concentration in the slurry 20.

5 The probe 26 measures the carbon dioxide content in the gas above the sulphide mineral slurry 20. The probe 26 provides a control signal to a control device 48 which, in turn, controls the operation of the valve 40 in order to control the addition of carbon dioxide from the source 34 to a gas stream flowing to the sparger 44.

The air flow rate from the source 36 to the sparger 44 is controlled by means of the valve 42. Normally the valve is set to provide a more or less constant flow of air from the source 36 to the sparger and the additions of oxygen and carbon dioxide to the air stream are controlled by the valves 38 and 40 respectively. Although this is a preferred approach to adjusting the oxygen and carbon dioxide contents in the air flow to the sparger other techniques can be adopted. For example it is possible, although with a lower degree of preference, to adjust the air stream flow rate and to mix the adjustable air stream with a steady supply of oxygen and a variable supply of carbon dioxide, or vice versa. Another possibility is to have two separate air stream flows to which are added oxygen and carbon dioxide respectively. Irrespective of the technique which is adopted the objective remains the same, namely to control the additions of oxygen and carbon dioxide to the slurry 20.

Slurry 50 is fed from a slurry feed source 52 through a control valve 54 and through an inlet pipe 56 into the interior of the tank 18. The slurry feed rate may be maintained substantially constant, by appropriate adjustment of the valve 54, to ensure that slurry is supplied to the tank 18 at a rate which sustains an optimum leaching rate. The supplies of air, oxygen and carbon dioxide are then regulated, taking into account the substantially constant slurry feed rate, to achieve a desired dissolved oxygen concentration in the slurry 20 in the tank, and a desired carbon dioxide content in the gas 30 above the slurry. Although this is a preferred approach it is apparent that the slurry feed rate could be adjusted, in response to a signal from the probe 24, to achieve a desired dissolved oxygen concentration in the slurry. In other words the rate of oxygen addition to the slurry may be kept substantially constant and the slurry feed rate may be varied according to requirement.

Another variation which can be adopted is to move the probe 24 from a position at which it is immersed in the slurry to a position designated 24A at which it is located in the gas 30 above the level 28. The probe then measures the oxygen contained in the gas above the slurry i.e. the bioreactor off-gas. The oxygen content in the off-gas can also be used as a measure to control the dissolved oxygen concentration in the slurry, taking any other relevant factors into account.

Conversely it may be possible to move the carbon dioxide probe 26 (provided it is capable of measuring the dissolved carbon dioxide content) from a position at which it is directly exposed to the gas 30 to a position designated 26A at which it is immersed in the slurry in the tank. The signal produced by the probe at the position 26A is then used, via the control device 48, to control the addition of carbon dioxide from the source 34 to the air stream from the source 36.

Although the carbon dioxide source 34, which provides carbon dioxide in gas form, is readily controllable and represents a preferred way of introducing carbon into the slurry 20, it is possible to add suitable carbonate materials to the slurry 50 before feeding the slurry to the reactor. Carbonate material may also be added directly to the sulphide mineral slurry 20 in the reactor. In other cases though there may be sufficient carbonate in the sulphide mineral slurry so that it is not necessary to add carbon, in whatever form, to the slurry nor to control the carbon content in the slurry.

It is apparent from the foregoing description which relates to the general principles of the invention that the supply of oxygen to the slurry is monitored and controlled to provide a desired dissolved oxygen concentration level in the slurry 20. This can be done in a variety of ways e.g. by controlling one or more of the following in an appropriate manner namely: the slurry feed rate, the air flow rate from the source 36, the oxygen flow rate from the source 32, and any variation of the foregoing.

The carbon dioxide flow rate is changed in accordance with the total gas flow rate to the sparger 44 in order to maintain a concentration in the gas phase, i.e. in the gas stream to the reactor, of from 0.5% to 5% carbon dioxide by volume. This carbon dioxide range has been found to maintain an adequate dissolved carbon dioxide concentration in the slurry, a factor which is important in achieving effective leaching.

The addition of oxygen to the sulphide mineral slurry 20 is controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. The upper threshold value depends on the genus and strain of microorganism used in the bioleaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Figure 1 illustrates the addition of oxygen from a source 32 of pure oxygen. The pure oxygen can be mixed with air from the source 36. Any other suitable gas can be used in place of the air. The addition of oxygen to air results to what is referred to in this specification as oxygen enriched gas i.e. a gas with an oxygen content in excess of 21% by volume. It is possible though to add oxygen substantially in pure form directly to the slurry. As used herein pure oxygen is intended to mean a gas stream which contains more than 85% oxygen by volume.

The temperature in the bioleach reactor or vessel may be controlled in any appropriate way using techniques which are known in the art. In one example the tank 18 is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry 20 is regulated using an internal cooling system 70 which includes a plurality of heat exchanger cooling coils 72 connected to an external heat exchanger 74.

The vessel 18 may be substantially sealed by means of a lid 80. Small vents 82 are provided to allow for the escape of off-gas. The off-gas may, if required, be captured or treated in any appropriate way before being released to atmosphere. Alternatively, according to requirement, the tank 18 may be open to atmosphere.

The microorganisms chosen for the leaching process will determine the leaching temperature, and vice versa. The applicant has found that a preferred operating temperature is above 60°C, for example in the range of 60°C to 85°C. In this range thermophilic microorganisms, in any appropriate combination, are employed. In the range of from 45°C to 60°C, on the other hand, moderate thermophiles are employed while at temperatures below 45°C mesophiles are used. These microorganisms may, for example, be chosen from those referred to hereinbefore.

Although the benefit of adding oxygen to the slurry which is to be leached, by making use of oxygen enriched air or, more preferably, by making use of substantially pure oxygen i.e. with an oxygen content in excess of 85%, is most pronounced at high temperatures at which greater leaching rates are possible, a benefit is nonetheless to be seen when oxygen enriched air or substantially pure oxygen is added to the slurry at lower temperatures, of the order of 40°C or even lower. At these temperatures the leaching rates are slower than

at elevated temperatures and although an improvement results from using oxygen enriched air the cost thereof is generally not warranted by the relatively small increase in leaching rate.

Test Results

5 The importance of maintaining an adequate supply of oxygen and hence a sufficiently high dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is shown in the results presented in Figure 2. If the dissolved oxygen concentration is allowed to drop below 1.5 ppm, and particularly below 1.0 ppm, biooxidation becomes unstable, which is indicated by higher iron(II) concentrations in solution, of greater than 2 g/l. At consistent levels of biooxidation, achieved by maintaining a dissolved oxygen concentration above 1.5 ppm, in this experiment, iron(II) is rapidly oxidised to iron(III), and iron(II) concentrations remain generally below 1.0 g/l.

5 The results presented in Figure 2 were obtained from operation of a first or primary reactor of a continuous pilot plant treating a chalcopyrite concentrate at a feed solids concentration of 10% by mass and a temperature of 77°C, with *Sulfolobus*-like archaea.

The effect of increasing the oxygen content of the feed gas to a bioreactor and controlling the dissolved oxygen concentration, in accordance with the principles of the invention, was tested in an experiment using a 5m³ bioreactor which was operated with a continuous pyrite or blended pyrrhotite and pyrite flotation concentrate feed, at a temperature of about 77°C, using a mixed culture of *Sulfolobus*-like archaea and a solids density of 10% by mass. The carbon dioxide content in the bioleach inlet gas was controlled at a level of between 1 and 1.5 % by volume. The dissolved oxygen concentration was generally within the range 0.4×10^{-3} kg/m³ to 3.0×10^{-3} kg/m³. The results of the experiment are presented in Figure 3.

From the graphs presented in Figure 3 it is clear that, when sparging with air (enriched with carbon dioxide: 20.7% oxygen and 1.0% carbon dioxide), the maximum oxygen demand (directly proportional to the sulphide oxidation duty) was limited to 11.3 kg/m³/day, since the dissolved oxygen concentration which was achievable using air only (i.e. not enriched with oxygen) was just sufficient to maintain microorganism growth.

By controlling the oxygen content of the inlet gas, the oxygen addition rate, and the dissolved oxygen concentration in the slurry in the range of $0.4 \times 10^{-3} \text{ kg/m}^3$ to $3.0 \times 10^{-3} \text{ kg/m}^3$, the oxygen demand, i.e. the sulphide mineral oxidation rate, was increased dramatically. The dissolved oxygen concentration was controlled to a low value, but above the minimum limit for successful microorganism growth, so that the utilisation of oxygen was maximised. The results show the oxygen demand, or sulphide oxidation duty, was increased by over threefold. Thus by increasing the oxygen content in the inlet gas from 20.7% to a maximum of 90.8% the specific oxygen demand was increased from $11.3 \text{ kg/m}^3/\text{day}$ to $33.7 \text{ kg/m}^3/\text{day}$. In addition, by controlling the dissolved oxygen concentration to a low value, but above the minimum value for sustained microorganism growth, the oxygen utilisation was maximised. The oxygen utilisation showed a general increase with an increase in the oxygen content of the inlet gas from 29% (for an inlet gas oxygen content of 20.7%) to 91% (for inlet gas containing 85.5% oxygen).

The high oxygen utilisations achieved of well over 60% are much better than expected. Analysis of the results indicates that the oxygen mass transfer coefficient (M), as defined by equation (1), is significantly and unexpectedly enhanced for operation of the bioreactor at a high temperature (77°C) and with a high oxygen content in the inlet gas (from 29% to 91% in the experiment). In fact, the oxygen mass transfer coefficient (M) is increased by a factor of 2.69, on average, compared to the applicant's design value. This enhancement is after considering the improvement in the mass transfer coefficient due to temperature, which would be expected to increase the value of M by a factor of 1.59 for a temperature increase from 42°C to 77°C , according to the temperature correction factor proposed by Smith et al ⁽⁵⁾. This correction factor has been demonstrated experimentally to be valid for a temperature in the range of from 15°C to 70°C ⁽⁶⁾

The determination of the enhanced oxygen mass transfer coefficient is shown from the results presented in Figure 4, where the oxygen demand divided by the design oxygen mass transfer coefficient (M_{design}) is plotted against the oxygen driving force, as defined in equation (1). The slope of the regression line plotted through the data indicates the enhancement in the oxygen mass transfer coefficient by a factor of 2.69.

Process Example

The inventive principles in the preceding section have been described in the context of sulphide minerals in general and, as will be appreciated by those skilled in the art, these principles can be applied to nickel bearing sulphide minerals in particular.

Figure 5 of the accompanying drawings is a process flow chart illustrating the use of method of the invention for recovering nickel.

In Figure 5 the plant 10 which is shown in Figure 1 and which is described hereinbefore bears the same reference numeral. The oxygen and carbon dioxide sources bear the reference numerals 32 and 34 respectively. The nickel sulphide slurry is labelled with the numeral 50.

The slurry 50 is fed to the plant 10 which contains one or more bioleach reactors using oxygen enriched gas or pure oxygen, labelled 32, as the oxidant. The oxygen concentration in the reactor is controlled in the manner which has been described hereinbefore depending on the type of microorganism used.

The bioleaching process produces a bioleach residue slurry 100 which contains solubilised nickel, and iron predominantly in the ferric state.

Optionally at this point the bioleach residue slurry 100 may be subjected to a liquid/solid separation step 102 which produces waste 104 and solution 104 from which copper 108, a metal commonly associated with nickel, is recovered by solvent extraction and electrowinning 110. Raffinate 111 from the solvent extraction step is returned to the main process flow stream.

Referring again to the main process flow stream iron in the bioleach residue slurry is removed by precipitation 112 brought about by the addition of limestone 114. Optionally, if there is insufficient carbonate in the nickel concentrate 50, some of the carbon dioxide 116 generated in the iron precipitation may be introduced into the

slurry in the plant 10 in any appropriate way for example by being blended with the oxygen 32, by being added to the carbon dioxide source 34, or by being injected directly into the slurry.

Slurry 118 produced by the iron precipitation 112 is subjected to a liquid/solid separation step 120 to produce solids 122 which are disposed of and a solution 124 which is fed to a nickel solvent extraction step 126. Strip liquor 128 from the solvent extraction step 126 is obtained by stripping the loaded solvent with anolyte 130 from a nickel electrowinning step 132. The pH of the nickel solvent extraction loading stage is maintained using a suitable alkali 134.

Raffinate 136 produced during the solvent extraction step may be disposed of or recycled (138).

The impure nickel strip liquor 128 is sent to another solvent extraction step 140 where cobalt and other impurities are removed. The pH of the cobalt solvent extraction loading stage is maintained using a suitable alkali 142. Dilute sulphuric acid 144 is used to strip the organic solvent to produce an impure cobalt sulphate solution 146 for further purification.

The cobalt solvent extraction raffinate 148 forms an advance electrolyte for the nickel electrowinning stage 132 in which nickel cathodes 150 are produced.

Oxygen gas 152 generated at the anode during the electrowinning process 128 may be recycled to the source 32, or directly into the slurry in the plant 10, to supplement the oxygen requirements during the bioleaching process.

The method of the invention is not limited to the use of an electrowinning process for the recovery of nickel. Other techniques may be employed. For example pressure hydrogen reduction (PHR) may be used as the production method of nickel. As the PHR system is known in the art it is not further described herein. Its use is however indicated symbolically by means of a block 160 as an alternative to the electrowinning process 132. In the PHR process nitrogen gas is required for purging the nickel reduction autoclaves during the production cycle of nickel powder. If the oxygen source 32 is used on site then, as a by product, nitrogen gas

162 is generated. This gas may be used, as indicated, for purging the autoclaves used for nickel powder production in the PHR process.

As has been indicated it is possible to operate the bioleach plant 10 in parallel to a pressure acid leaching (PAL) system which is used for the recovery of nickel from lateritic ores. This option is illustrated by means of a block labelled 170 which represents a pressure acid leaching installation for the recovery of nickel from lateritic ores.

The volumes arising downstream of PAL processes are roughly an order of magnitude higher than the mass of nickel sulphide concentrates arising from sulphide nickel mines. Since the residue from the bioleach plant 10 is similar in nature to the residue from the PAL installation 170, i.e. each residue has a low pH, and contains solubilised nickel and iron, it is advantageous to treat the bioleach residue for nickel and cobalt recovery using the larger PAL downstream process equipment. Thus combining a nickel sulphide bioleach residue slurry (100) with a PAL residue slurry and treating the streams together thereafter brings about considerable economies of scale in terms of capital and operating costs.

Pilot Plant Test Work

Bioleach pilot plant test work was completed, using a predominantly pentlandite concentrate assaying 11.9% nickel, on a 0.849 m³ pilot plant consisting of 5 reactors configured as 1 primary reactor followed by 4 secondary reactors in series. The total primary volume was 237l and the total secondary volume was 612l. All test work was carried out at between 65°C to 68°C using a feed slurry containing 15% solids. The microorganism used was a mixed culture of *Sulfolobus*-like archaea. The oxygen utilisation results obtained in the primary stage during the test work, using analysis of inlet and outlet gas mixtures, are shown in Table 3.

Table 3 : Primary Reactor Nickel Dissolution and Oxygen Uptake Results for Thermophile Pilot Test Work

Retention Days	Ni Dissolution %	Specific S ²⁻ Oxidation Rate kg/m ³	Oxygen Consumption Rate kg/m ³ /h
2.0	83.5	0.729	1.58

The results in Table 3 may be compared to mesophile results obtained at 40°C to 45°C. This test work was completed using the same concentrate as before, containing 11.9% nickel. The primary reactor in this test work had a volume of 60l , and the feed contained 15.9% solids. The results are shown in Table 4.

Table 4 : Primary Reactor Nickel Dissolution and Oxygen Uptake Results for Mesophile Bioleaching

Retention Days	Ni Dissolution %	Specific S ²⁻ Oxidation Rate kg/m ³	Oxygen Consumption Rate kg/m ³ /h
2.4	68.3	0.534	1.16

These results indicate about a 40% increase in specific sulphide oxidation rate when using thermophiles according to the method of the invention.

REFERENCES

1. Bailey, A.D., and Hansford, G.S., (1996), Oxygen mass transfer limitation of batch bio-oxidation at high solids concentration. *Minerals Eng.*, 7(23), pp293-303.
2. Myerson, A.S., (1981), Oxygen mass transfer requirements during the growth of *Thiobacillus ferrooxidans* on iron pyrite. *Biotechnol, Bioeng.*, Vol 23, pp1413.
3. Peter Greenhalgh, and Ian Ritchie, (1999); Advancing Reactor Design For The Gold Bioleach Process; Minproc Ltd. Biomine 99, 23-25 Aug 1999, Perth Australia. pp52-60.
4. Brock Biology of Microorganisms, Eight Edition, 1997.. Madigan M.T., Martinko J.M., Parker J., Prentia Hall International, Inc., London.
5. J.M. Smith, K van't Riet and J.C. Middleton, (1997), Scale-Up of Agitated Gas-Liquid Reactors for Mass Transfer, in Proceedings of the 2nd European Conference on Mixing, Cambridge, England, 30 March – 1 April 1997. pp.F4-51 – F4-66.
6. Boogerd, F. C., Bos, P., Kuenen, J. G., Heijnen, J. J. & Van der Lans, R. G. J.
M. Oxygen and Carbon Dioxide Mass Transfer and the Aerobic, Autotrophic Cultivation of Moderate and Extreme Thermophiles : A Case Study Related to the Microbial Desulfurization of Coal, *Biotech. Bioeng.*, 35, 1990. p. 1111 – 1119.
7. Mayze, R. (1999) An Engineering Comparison of the Three Treatment Flowsheets in WA Nickel Laterite Projects; Alta 1999 Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum.

CLAIMS

1. A method of recovering nickel from a nickel bearing sulphide mineral slurry which includes the steps of:
 - (a) subjecting the slurry to a bioleaching process,
 - (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry, and
 - (c) recovering nickel from a bioleach residue of the bioleaching process
2. A method according to claim 1 wherein copper is removed from the bioleach residue before recovering nickel therefrom.
3. A method according to claim 2 wherein cobalt is removed from the bioleach residue before recovering nickel therefrom.
4. A method according to any one of claims 1 to 3 which includes the step of removing iron from the bioleach residue before recovering nickel therefrom.
5. A method according to claim 4 wherein the iron is precipitated from the bioleach residue by the addition of limestone to the residue.
6. A method according to claim 5 wherein carbon dioxide generated in the iron precipitation step is fed to the feed gas of step (b) or directly to the slurry.
7. A method according to any one of claims 1 to 6 wherein, in step (c), nickel is recovered using a solvent extraction and electrowinning process.
8. A method according to claim 7 wherein oxygen generated during the nickel electrowinning is fed to the feed gas of step (b) or directly to the slurry.

9. A method according to any one of claims 1 to 6 wherein, in step (c), nickel is recovered using a pressure hydrogen reduction process and nitrogen, produced during the generation of the feed gas supplied to the slurry in step (b), is used for purging autoclaves used for nickel powder production in the pressure hydrogen reduction process.

10. A method according to any one of claims 1 to 9 which is operated in parallel to a process for recovering nickel from lateritic ores by pressure acid leaching to produce a nickel laterite ore slurry and which includes the step of adding the bioleach residue to the nickel laterite residue slurry before carrying out step (c).

11. A method according to any one of claims 1 to 10 wherein the feed gas contains in excess of 85% oxygen by volume.

12. A method according to any one of claims 1 to 11 which includes the step of maintaining the dissolved oxygen concentration in the slurry within a desired range

13. A method according to claim 12 wherein the said dissolved oxygen concentration is maintained in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

14. A method according to any one of claims 1 to 13 which includes the step of controlling the carbon content of the slurry.

15. A method according to any one of claims 1 to 14 which includes the step of controlling the carbon dioxide content of the slurry in the range of from 0.5% to 5.0% by volume.

16. A method according to any one of claims 1 to 15 which includes the step of bioleaching the slurry at a temperature in excess of 40°C .

17. A method according to claim 16 wherein the said temperature is in the range of from 40°C to 100°C .

18. A method according to claim 17 wherein the said temperature is in the range of from 60°C to 85°C.
19. A method according to any one of claims 1 to 15 which includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms.
20. A method according to claim 19 wherein the microorganisms are selected from the following genus groups: *Acidithiobacillus*; *Thiobacillus*; *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.
21. A method according to claim 19 or 20 wherein the said microorganisms are selected from the following species: *Acidithiobacillus caldus* (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*); *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus acidophilus*); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.
22. A method according to any one of claims 1 to 15 which includes the step of bioleaching the slurry at a temperature of from 45°C to 60°C using moderate thermophile microorganisms.
23. A method according to claim 22 wherein the microorganisms are selected from the following genus groups: *Acidithiobacillus* (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferropasma* (*Ferriplasma*); and *Alicyclobacillus*.
24. A method according to claim 22 or 23 wherein the said microorganisms are selected from the following species: *Acidithiobacillus caldus* (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferropasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.
25. A method according to any one of claims 1 to 15 which includes the step of bioleaching the slurry at a temperature of from 60°C to 85°C using thermophilic microorganisms.

26. A method according to claim 25 wherein the microorganisms are selected from the following genus groups: *Acidothermus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma* (*Ferriplasma*); *Thermoplasma*; and *Picrophilus*.
27. A method according to claim 25 or 26 wherein the said microorganisms are selected from the following species: *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.
28. A method of recovering nickel from a slurry containing nickel bearing sulphide minerals which includes the steps of:
- (a) bioleaching the slurry using suitable bacteria at a temperature in excess of 40°C,
 - (b) controlling the dissolved oxygen concentration in the slurry within a predetermined range, and
 - (c) recovering nickel from a bioleach residue produced in step (a).
29. A method according to claim 28 wherein the said dissolved oxygen concentration is controlled by controlling the supply of oxygen to the slurry.
30. A method according to claim 29 wherein the oxygen is supplied to the slurry in the form of oxygen enriched gas or substantially pure oxygen.
31. A method according to any one of claims 28 to 30 wherein the said temperature is in the range of from 60°C to 85°C.
32. A method of enhancing the oxygen mass transfer coefficient from a gas phase to a liquid phase in a nickel bearing sulphide mineral slurry which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume, to the slurry.

33. A method according to claim 32 wherein the feed gas contains in excess of 85% oxygen by volume.
34. A method according to claim 32 or 33 which includes the step of raising the temperature of the slurry.
35. A method of bioleaching an aqueous slurry containing nickel bearing sulphide minerals which includes the steps of:
- (a) bioleaching the slurry at a temperature above 40°C, and
 - (b) maintaining the dissolved oxygen concentration in the slurry in the range of from 0.2×10^{-3} kg/m³ to 10×10^{-3} kg/m³.
36. A method according to claim 35 wherein the dissolved oxygen concentration in the slurry is maintained by supplying gas containing in excess of 21% oxygen by volume to the slurry.
37. A method according to claim 35 or 36 wherein the temperature is in the range of from 60°C to 85°C.
38. A plant for recovering nickel from a nickel bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a nickel bearing sulphide mineral slurry to the vessel, an oxygen source, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measured dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry within a predetermined range, and a recovery system which recovers nickel from a bioleach residue from the reactor vessel.
39. A plant according to claim 38 which includes an installation for recovering nickel from lateritic ores by pressure acid leaching to produce a nickel laterite residue slurry which is combined with the said bioleach residue from the reactor vessel, and the combined slurry and residue are fed to the said recovery system.

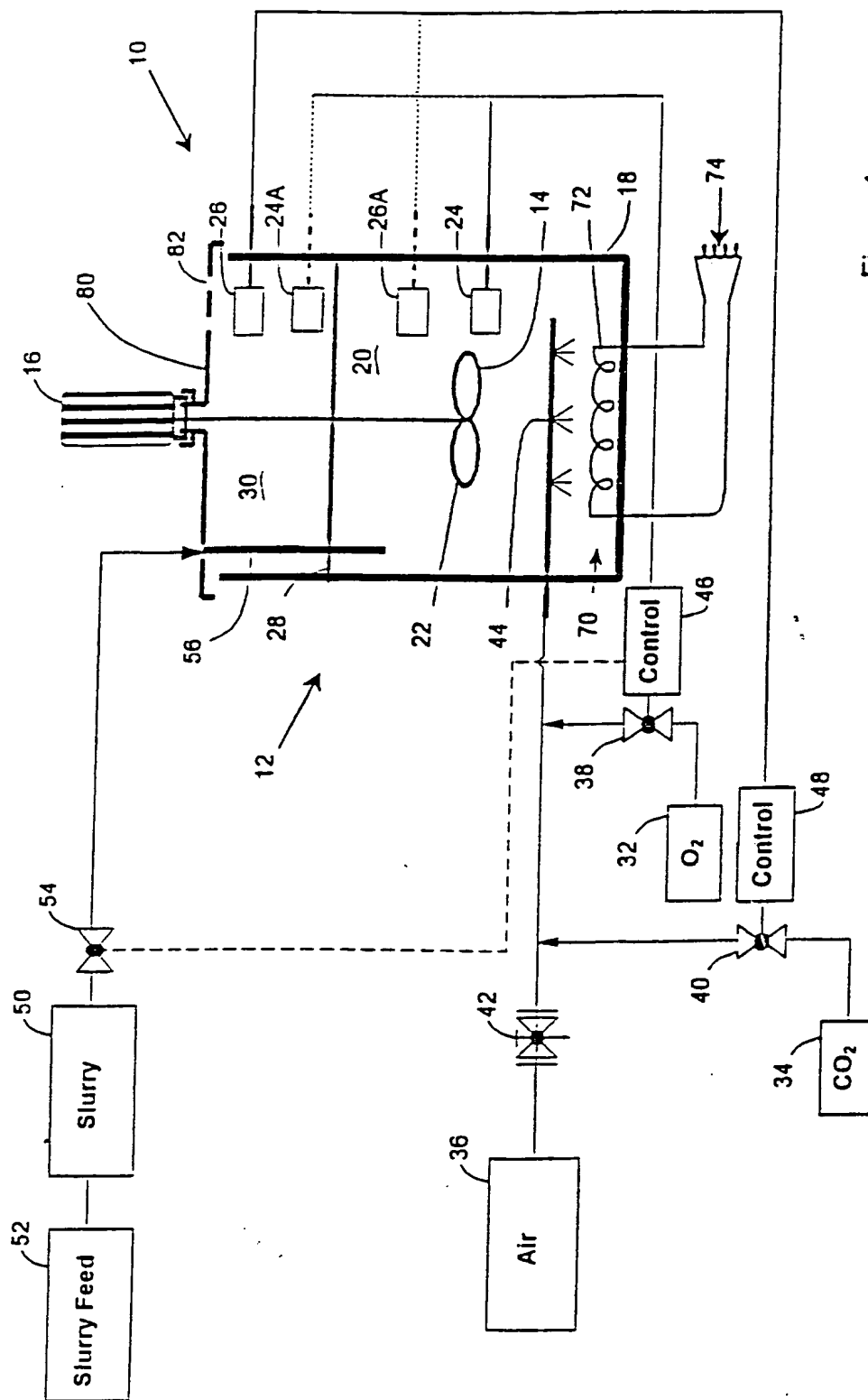


Figure 1

Ferrous Concentration vs. Dissolved Oxygen Concentration

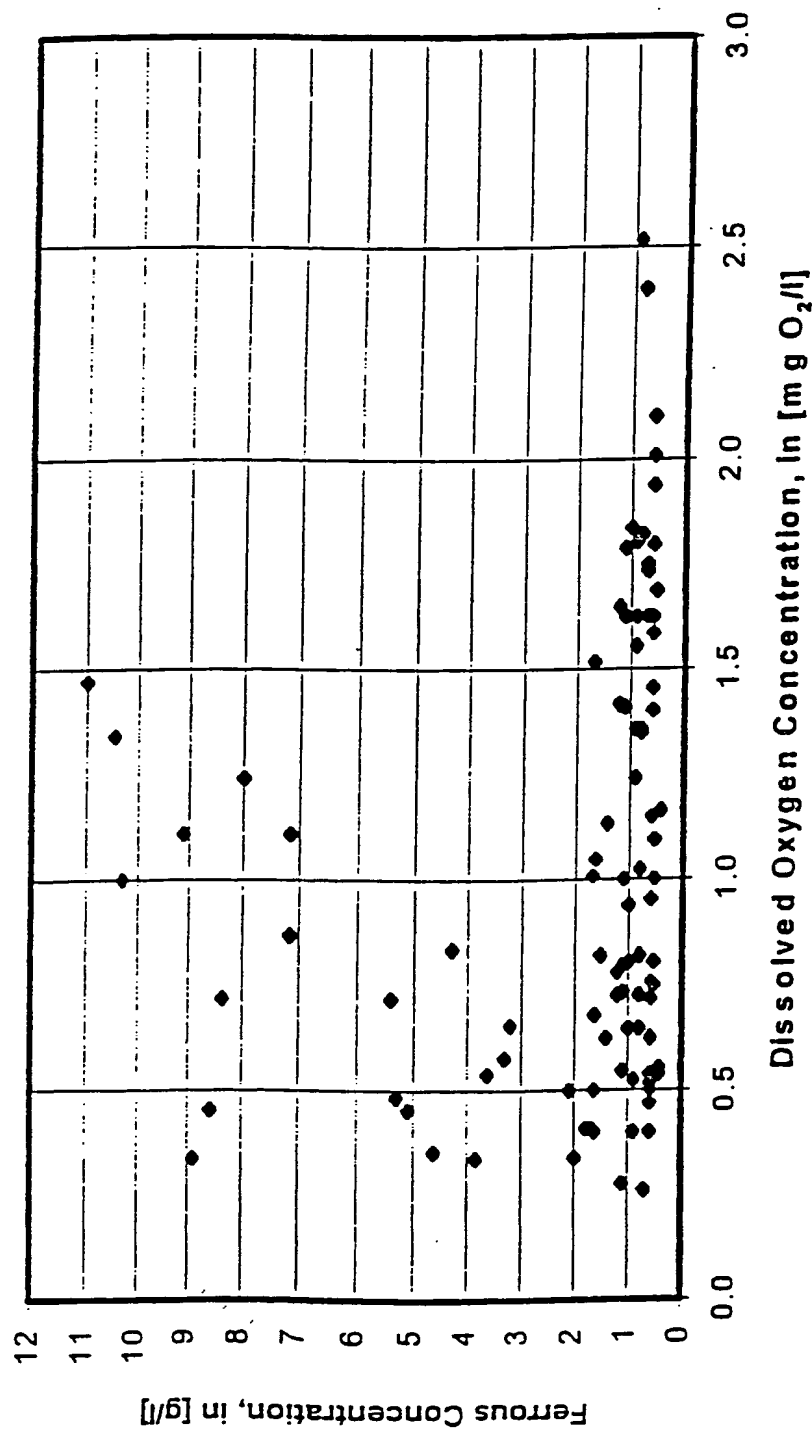


Figure 2 Results Showing The Effect of Reduced Microbial Oxidation On Iron(II) Concentration Levels In Solution As A Result Of Operating At Low Dissolved Oxygen Concentrations

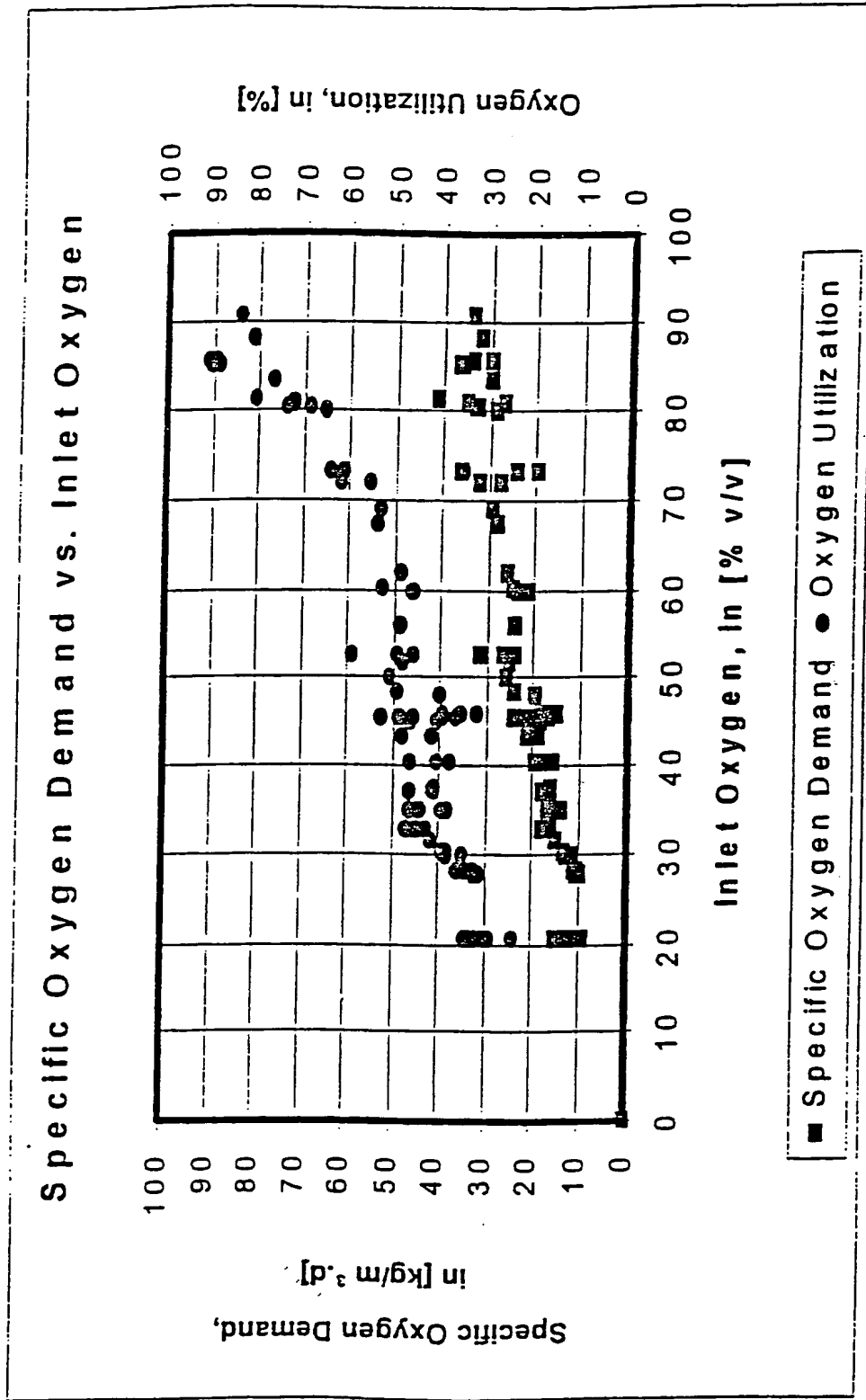


Figure 3 Results Showing The Increase In Specific Oxygen Demand and Oxygen Utilisation Achieved By Increasing The Oxygen Content Of The Inlet Gas Under Controlled Conditions By The Method Of The Invention

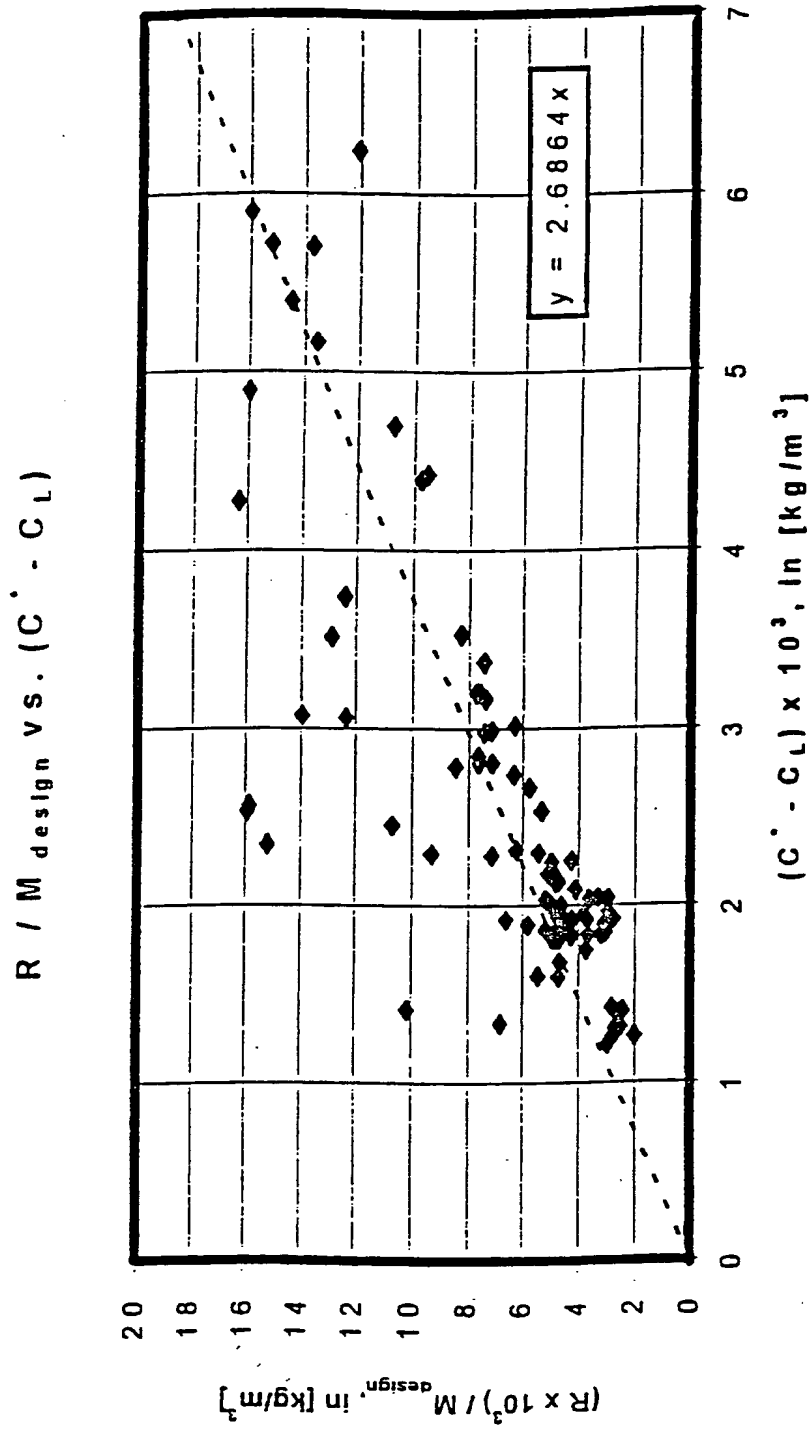


Figure 4 Results Demonstrating The Enhancement Of The Oxygen Mass Transfer Coefficient

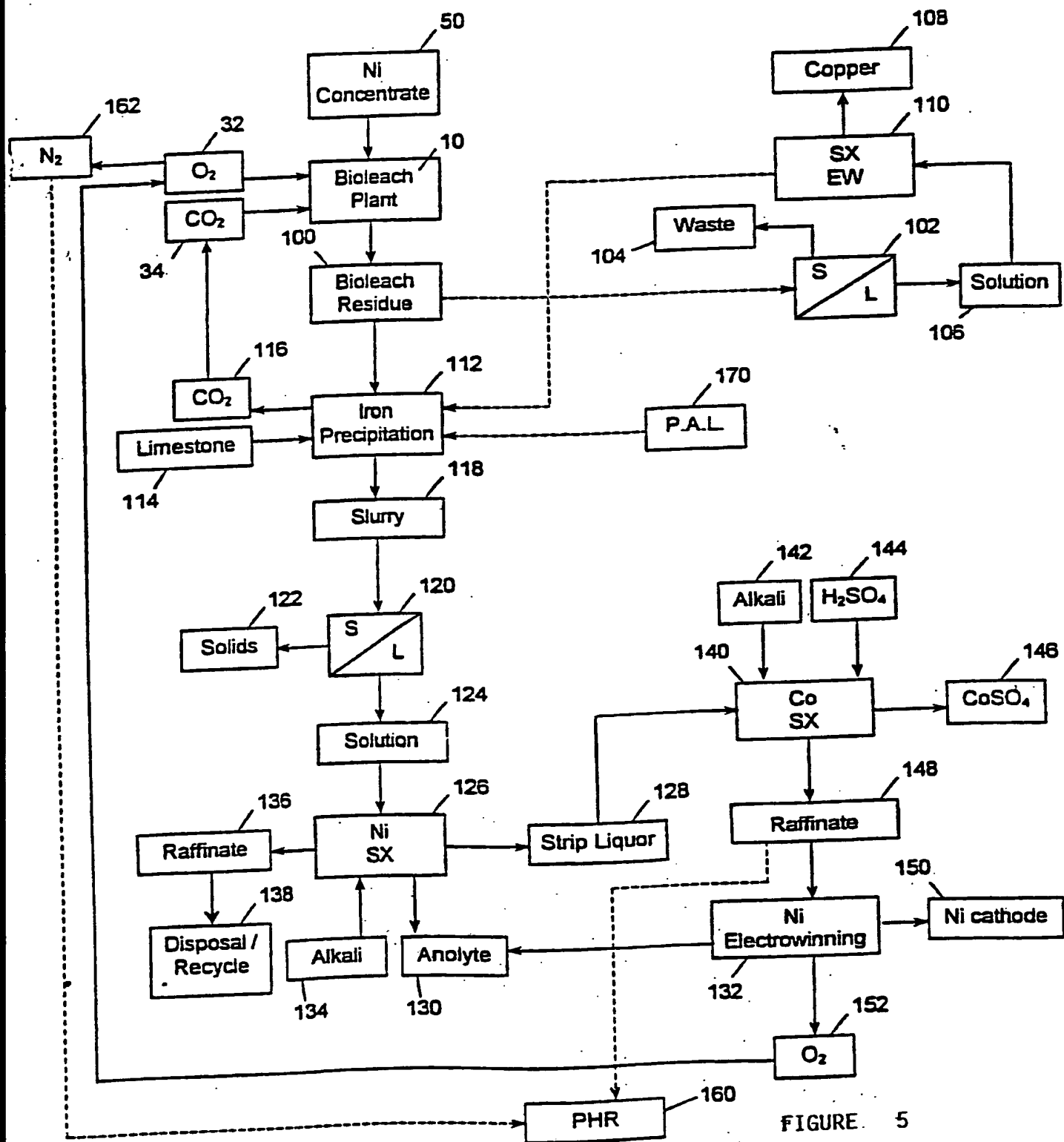


FIGURE 5

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 225 256 A (TOLMIN MINERAL TECHNOLOGIES NV) 30 May 1990 (1990-05-30) page 1, line 15 -page 2, line 13; claims 1,3-6,8-13,20-23; figures 1-8 page 6, line 19 -page 7, line 20	1-5,7, 10-39
Y	US 5 007 620 A (EMMETT JR ROBERT C ET AL) 16 April 1991 (1991-04-16) column 15, line 49 - line 65; figures 1-7,20,21,33 column 19, line 3 - line 12 column 21, line 45 - line 53	1-5,7, 10-39
Y	WO 98 26100 A (BHP MINERALS INT INC) 18 June 1998 (1998-06-18) example 2	1-5,7, 10-37
	--- -/--	

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

4 December 2000

Date of mailing of the international search report

12/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Bombeke, M

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication of the appropriate of the relevant passages	Relevant to claim No.
Y	GB 2 291 870 A (GENCOR LTD) 7 February 1996 (1996-02-07) page 4 -page 6 ----	1,4,5,7, 19-21
Y	WO 99 09226 A (JONES DAVID L ;COMINCO ENG SERVICES (CA)) 25 February 1999 (1999-02-25) figures 2-4 ----	2-5,7, 10,39
Y	EP 0 808 910 A (UNIV MICHIGAN TECH) 26 November 1997 (1997-11-26) column 8, line 3 - line 25; figure 1 ----	38
P,X	WO 00 29629 A (MILLER PAUL CHARLES ;RHODES MIKE (AU); WINBY RICHARD (AU); BACTECH) 25 May 2000 (2000-05-25) page 3, line 14 -page 4, line 26 -----	1,11. 16-34

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2225256 A	30-05-1990	AU 630889 B	12-11-1992
		AU 4262989 A	12-04-1990
		US 5021069 A	04-06-1991
		ZA 8907627 A	25-09-1991
US 5007620 A	16-04-1991	US 4974816 A	04-12-1990
		US 4732608 A	22-03-1988
		AT 78240 T	15-08-1992
		AU 607901 B	21-03-1991
		AU 6858087 A	13-08-1987
		CA 1329989 A	07-06-1994
		DE 3780452 A	20-08-1992
		DE 3780452 D	20-08-1992
		DE 3780452 T	11-03-1993
		EP 0294387 A	14-12-1988
		ES 2001827 A	16-06-1988
		FI 883604 A	01-08-1988
		GR 870202 A	05-06-1987
		JP 63502796 T	20-10-1988
		NZ 219219 A	26-04-1990
		WO 8704694 A	13-08-1987
		US 5057284 A	15-10-1991
		US 5227136 A	13-07-1993
		ZW 15687 A	28-10-1987
		BR 8700558 A	08-12-1987
		US 4968008 A	06-11-1990
		US 4728082 A	01-03-1988
		ZA 8606691 A	24-06-1987
		ZA 8700817 A	28-10-1987
		ZM 1587 A	28-03-1988
		ZW 11686 A	18-02-1987
WO 9826100 A	18-06-1998	US 5626648 A	06-05-1997
		AU 720713 B	08-06-2000
		AU 1288697 A	03-07-1998
		BR 9612802 A	28-03-2000
		EP 0948655 A	13-10-1999
GB 2291870 A	07-02-1996	AU 689598 B	02-04-1998
		AU 2726295 A	15-02-1996
		CA 2155051 A	02-02-1996
		FI 953487 A	02-02-1996
		ZA 9506204 A	12-03-1996
WO 9909226 A	25-02-1999	AU 8796398 A	08-03-1999
		AU 8847598 A	08-03-1999
		BR 9811945 A	22-08-2000
		WO 9909225 A	25-02-1999
		CN 1267338 T	20-09-2000
		CN 1271392 T	25-10-2000
		EP 1012351 A	28-06-2000
		EP 1012352 A	28-06-2000
		NO 20000727 A	21-03-2000
EP 0808910 A	26-11-1997	US 5827701 A	27-10-1998
		AU 725634 B	19-10-2000
		AU 2141197 A	27-11-1997
		CA 2205151 A	21-11-1997

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0808910 A		JP 10113694 A US 6043022 A ZA 9704368 A	06-05-1998 28-03-2000 24-08-1998
WO 0029629 A	25-05-2000	AU 1141400 A	05-06-2000

RECOVERY OF NICKEL FROM NICKEL BEARING SULPHIDE MINERALS BY BIOLEACHING

BACKGROUND OF THE INVENTION

5 This invention relates to the recovery of nickel from nickel bearing sulphide minerals.

Commercial bioleach plants which are currently in operation treating sulphide minerals, typically operate within the temperature range of 40°C to 50°C and rely on sparging air to the bioleach reactors to provide the required oxygen. Operation at this relatively low temperature and the use of air to supply oxygen, limit the
10 rate of sulphide mineral oxidation that can be achieved.

The use of high temperatures between 50°C and 100°C greatly increases the rate of sulphide mineral leaching.

15 The solubility of oxygen is however limited at high temperatures and the rate of sulphide mineral leaching becomes limited. In the case of using air for the supply of oxygen, the effect of limited oxygen solubility is such that the rate of sulphide mineral leaching becomes dependent on and is limited by the rate of oxygen transfer from the gas to the liquid phase ^(1,2).

20 The bioleaching of nickel sulphide bearing minerals is similarly problematic and to the applicant's knowledge no commercial nickel bioleaching plants are in operation.

SUMMARY OF THE INVENTION

25

According to one aspect of the invention there is provided a method of recovering nickel from a nickel bearing sulphide mineral slurry which includes the steps of:

- (a) subjecting the slurry to a bioleaching process,
- (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry, and
30 (c) recovering nickel from a bioleach residue of the bioleaching process.

If the slurry contains copper then preferably copper is removed from the bioleach residue before recovering nickel therefrom.

The method may include the step of recovering cobalt from the bioleach residue before recovering nickel therefrom.

Iron may also be removed from the bioleach residue before recovering nickel therefrom. The iron may be precipitated from the bioleach residue by the addition of limestone to the residue, or in any other suitable way. Carbon dioxide generated in the iron precipitation step may be fed to the feed gas of step (b) or directly to the slurry.

In step (c) nickel may be recovered using any appropriate technique. Use may for example be made of a solvent extraction and electrowinning process. In this instance oxygen generated during the nickel electrowinning step may be fed to the feed gas of step (b) or directly to the slurry.

It is also possible to recover nickel, in step (c), using a pressure hydrogen reduction process. In this case nitrogen, produced during the generation of the feed gas which is supplied to the slurry in step (b), may be used for purging autoclaves used for nickel powder production in the pressure hydrogen reduction process.

The introduction of pressure acid leaching (PAL) for the recovery of nickel from lateritic ores opens up additional opportunities for bioleaching of nickel bearing sulphides. The volumes arising down stream of PAL processes are roughly an order of magnitude higher than the mass of nickel sulphide concentrates arising from sulphide nickel mines (approximately 1- 3 million tonnes per annum versus approximately 20-200 thousand tonnes per annum).

Since residues from both processes are similar in nature (low pH, solubilised nickel and iron) it is advantageous to treat the bioleach residue for nickel and cobalt recovery using the larger PAL downstream process equipment. Thus feeding a nickel sulphide bioleach residue slurry into a PAL residue slurry and

treating both streams together thereafter would bring about considerable economies of scale in terms of capital and operating costs.

Thus the invention also extends to operating the aforementioned method in parallel to a process for recovering nickel from lateritic ores by pressure acid leaching to produce a nickel laterite residue slurry and then adding the bioleach residue to the nickel laterite ore slurry before carrying out step (c).

As used herein the expression "oxygen enriched gas" is intended to include a gas, e.g. air, which contains in excess of 21% oxygen by volume. This is an oxygen content greater than the oxygen content of air. The expression "pure oxygen" is intended to include a gas which contains in excess of 85% oxygen by volume.

Preferably the feed gas which is supplied to the slurry contains in excess of 85% oxygen by volume i.e. is substantially pure oxygen.

The method may include the step of maintaining the dissolved oxygen concentration in the slurry within a desired range which may be determined by the operating conditions and the type of microorganisms used for leaching. The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation, is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. On the other hand if the dissolved oxygen concentration is too high then microorganism growth is inhibited. The upper threshold concentration also depends on the genus and strain of microorganism used in the leaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Thus, preferably, the dissolved oxygen concentration in the slurry is maintained in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

The method may include the steps of determining the dissolved oxygen concentration in the slurry and, in response thereto, of controlling at least one of the following: the oxygen content of the feed gas, the rate of supply of the feed gas to the slurry, and the rate of feed of slurry to a reactor.

The dissolved oxygen concentration in the slurry may be determined in any appropriate way, e.g. by one or more of the following: by direct measurement of the dissolved oxygen concentration in the slurry, by measurement of the oxygen content in gas above the slurry, and indirectly by measurement of the oxygen content in off-gas from the slurry, taking into account the rate of oxygen supply, whether in gas enriched or pure form, to the slurry, and other relevant factors.

The method may include the step of controlling the carbon content of the slurry. This may be achieved by one or more of the following: the addition of carbon dioxide gas to the slurry, and the addition of other carbonaceous material to the slurry.

The method may extend to the step of controlling the carbon dioxide content of the feed gas to the slurry in the range of from 0.5% to 5% by volume. A suitable figure is of the order of 1% to 1.5% by volume. The level of the carbon dioxide is chosen to maintain high rates of microorganism growth and sulphide mineral oxidation.

The bioleaching process is preferably carried out at an elevated temperature. As stated hereinbefore the bioleaching rate increases with an increase in operating temperature. Clearly the microorganisms which are used for bioleaching are determined by the operating temperature and vice versa. As the addition of oxygen enriched gas or substantially pure oxygen to the slurry has a cost factor it is desirable to operate at a temperature which increases the leaching rate by an amount which more than compensates for the increase in operating cost. Thus, preferably, the bioleaching is carried out at a temperature in excess of 40°C.

The bioleaching may be carried out at a temperature of up to 100°C or more and preferably is carried out at a temperature which lies in a range of from 60°C to 85°C.

In one form of the invention the method includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms. These microorganisms may, for example, be selected from the following genus groups:

Acidithiobacillus (formerly *Thiobacillus*); *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.

In order to operate at this temperature the said microorganisms may, for example, be selected from the following species:

Acidithiobacillus caldus (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*);
Acidithiobacillus ferrooxidans (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus*
5 *acidophilus*); *Thiobacillus prosperus*; *Leptospirillum ferrooxidans*; *Ferromicrobium acidophilus*; and
Acidiphilium cryptum.

If the bioleaching step is carried out at a temperature of from 45°C to 60°C then moderate thermophile microorganisms may be used. These may, for example, be selected from the following genus groups:

10 *Acidithiobacillus* (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma* (*Ferriplasma*); and
Alicyclobacillus.

Suitable moderate thermophile microorganisms may, for example, be selected from the following species:

Acidithiobacillus caldus (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus*
15 *acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*;
Thermoplasma acidophilum; and *Alicyclobacillus acidocaldrius*.

It is preferred to operate the leaching process at a temperature in the range of from 60°C to 85°C using thermophilic microorganisms. These may, for example, be selected from the following genus groups:

20 *Acidothermus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma* (*Ferriplasma*); *Thermoplasma*; and
Picrophilus.

Suitable thermophilic microorganisms may, for example, be selected from the following species:

Sulfolobus metallicus; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*;
25 *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*;
and *Picrophilus oshimae*.

The slurry may be leached in a reactor tank or vessel which is open to atmosphere or substantially closed. In the latter case vents for off-gas may be provided from the reactor.

According to a different aspect of the invention there is provided a method of recovering nickel from a slurry containing nickel bearing sulphide minerals which includes the steps of bioleaching the slurry using a suitable microorganism at a temperature in excess of 40°C, controlling the dissolved oxygen concentration in the slurry within a predetermined range, and recovering nickel from a bioleach residue.

5

The said dissolved oxygen concentration may be controlled by controlling the supply of oxygen to the slurry.

The oxygen may be supplied to the slurry in the form of oxygen enriched gas or substantially pure oxygen.

10 The said operating temperature is preferably above 60°C and may be in the range of 60°C to 85°C.

The invention also extends to a method of enhancing the oxygen mass transfer coefficient from a gas phase to a liquid phase in a nickel bearing sulphide mineral slurry which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume to the slurry.

15

The feed gas preferably contains in excess of 85% oxygen by volume.

20

The invention further extends to a method of bioleaching an aqueous slurry containing nickel bearing sulphide minerals which includes the steps of bioleaching the slurry at a temperature above 60°C and supplying gas containing in excess of 21% oxygen by volume to the slurry to maintain the dissolved oxygen concentration in the slurry in the range of from $0,2 \times 10^{-3}$ kg/m³ to 10×10^{-3} kg/m³.

25

The invention is also intended to cover a plant for recovering nickel from a nickel bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a nickel bearing sulphide mineral slurry to the vessel, an oxygen source, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measure of dissolved oxygen concentration, the supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry within a predetermined range, and a recovery system which recovers nickel from a bioleach residue from the reactor vessel.

The plant may include an installation for recovering nickel from lateritic ores by pressure acid leaching to produce a nickel laterite residue slurry which is combined with the said bioleach residue from the reactor, and the combined slurry and residue are fed to the said recovery system.

5

Various techniques may be used for controlling the supply of oxygen to the slurry and hence for controlling the dissolved oxygen concentration in the slurry at a desired value. Use may for example be made of valves which are operated manually. For more accurate control use may be made of an automatic control system. These techniques are known in the art and are not further described herein.

10

As has been indicated oxygen and carbon dioxide may be added to the slurry in accordance with predetermined criteria. Although the addition of these materials may be based on expected demand and measurement of other performance parameters, such as iron(II) concentration, it is preferred, however, to make use of suitable measurement probes to sample the actual values of the critical parameters.

15

For example use may be made of a dissolved oxygen probe to measure the dissolved oxygen concentration in the slurry directly. To achieve this the probe is immersed in the slurry. The dissolved oxygen concentration may be measured indirectly by using a probe in the reactor off-gas or by transmitting a sample of the off-gas, at regular intervals, to an oxygen gas analyser. Again it is pointed out that measuring techniques of this type are known in the art and accordingly any appropriate technique can be used.

20

A preferred approach to the control aspect is to utilise one or more probes to measure the dissolved oxygen concentration in the slurry, whether directly or indirectly. The probes produce one or more control signals which are used to control the operation of a suitable valve or valves, e.g. solenoid valves, automatically so that the supply of oxygen to an air stream which is being fed to the slurry is varied automatically in accordance with real time measurements of the dissolved oxygen concentration in the slurry

25

Although it is preferred to control the addition of oxygen to a gas stream which is fed to the slurry a reverse approach may be adopted in that the oxygen supply rate to the reactor vessel may be maintained

substantially constant and the rate of supply of the sulphide mineral slurry to the reactor vessel may be varied to achieve a desired dissolved oxygen concentration.

5 The invention is not limited to the actual control technique employed and is intended to extend to variations of the foregoing approaches and to any equivalent process.

Nickel bearing sulphide flotation concentrates frequently contain violarite and pyrrhotite and the method of the invention is of particular benefit, because both pyrrhotite and violarite have a high leaching rate, even at typical mesophile operating temperatures, which is further increased at the higher temperatures used with
10 moderate and extreme thermophiles. Thus the benefits of the invention, including a high specific reactor sulphide oxidation duty and reduced specific power requirement for oxidation, will be obtained during the bioleaching of nickel bearing sulphide concentrates, even at mesophile operating temperatures.

Nickel may be recovered from solution by any appropriate process, for example by solvent extraction applied
15 to the solution or by resin-in-pulp applied to the slurry, followed by electrowinning. The route adopted by Anaconda Nickel for treatment of leach liquors arising from nickel laterites at Murrin Murrin is also relevant i.e. by precipitation of a sulphide (using hydrogen sulphide) and refining of the sulphide precipitate by re-leaching, purification and hydrogen reduction⁽⁷⁾. The route adopted by Preston Resources on a similar solution to that produced at Murrin Murrin at the Cawse project is also applicable, by precipitating a hydroxide
20 (with magnesia), re-leaching, purification using solvent extraction and then electrowinning⁽⁷⁾. Lastly the same process used at Cawse but with the production of a nickel carbonate from the solvent extraction strip liquor, would be most suitable for the production of nickel rondelles by methods established by Queensland Nickel Limited.

25 If electrowinning is selected as the production method for nickel, the oxygen generated at the anode in the electrowinning process may be used to supplement that used in the bioleach process, reducing the capital and operating costs required for oxygen production.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention is further described by way of example with reference to the accompanying drawings in which:

Figure 1 is a schematic representation of a portion of a plant in which the invention is carried out,

5 Figures 2, 3 and 4 reflect various results and parameters obtained from operating a bioreactor using the principles of the invention, and

Figure 5 is a process flow sheet illustrating the recovery of nickel according to the invention, and various possible modifications.

10 DESCRIPTION OF PREFERRED EMBODIMENT

General Principles

The limitation of low oxygen solubility during bioleaching, using air, at high temperatures, which in turn limits
15 the rate of reaction, requires enrichment of the air with oxygen i.e. air with an oxygen content greater than 21% by volume, or the use of pure oxygen (defined as being greater than 85% oxygen by volume). The use of oxygen enriched air or pure oxygen overcomes the limited rate of reaction due to oxygen supply constraints, but has two major disadvantages:

- a) the provision of oxygen enriched air or pure oxygen is expensive and requires a high utilisation (>60%) of
20 the oxygen to warrant the additional expense ⁽³⁾; and
- b) if the oxygen level in solution becomes too high microorganism growth is prevented and sulphide mineral bioleaching stops ⁽⁴⁾.

Therefore, in order to realise the benefits of high rates of sulphide mineral leaching at high temperatures in
25 commercial bioleaching plants, the drawbacks of requiring expensive oxygen and the risk of failure if the dissolved oxygen levels become too high must be overcome.

The bioleaching of sulphide minerals at an elevated temperature results in a high rate of sulphide mineral oxidation, but is dependent on the supply of oxygen and carbon dioxide to maintain high rates of sulphide

mineral oxidation and of microorganism growth at adequate rates. The absorption of oxygen and carbon dioxide in the bioleaching reactor is limited, in each case, by the rate of mass transfer from the gas phase into the solution phase. For oxygen the rate of oxygen absorption is defined by equation (1) as follows:

$$R = M \cdot (C^* - C_L) \quad (1)$$

- 5 where:
- R = Oxygen demand as mass (kg) per unit volume (m^3) per unit time(s) ($kg/m^3/s$),
- M = Oxygen mass transfer coefficient in reciprocal seconds (s^{-1}),
- C^* = Saturated dissolved oxygen concentration as mass (kg) per unit volume (m^3) (kg/m^3),
and
- C_L = Dissolved oxygen concentration in solution as mass (kg) per unit volume (m^3)
10 (kg/m^3).

The factor $(C^* - C_L)$ is referred to as the oxygen driving force. A similar equation may be used to describe the rate of carbon dioxide supply to the solution. If the sulphide mineral oxidation rate is increased the oxygen demand increases proportionately. To meet a higher oxygen demand either the oxygen mass transfer
15 coefficient (M) or the oxygen driving force $(C^* - C_L)$ must be increased.

An increase in the oxygen mass transfer coefficient may be achieved by increasing the power input to the bioleach reactor mixer. This improves gas dispersion in the sulphide mineral slurry. With this approach, however, an increase in the oxygen mass transfer coefficient of, for example, 40% requires an increase in the
20 power input to the mixer by a factor of as much as 200%, with a commensurate increase in operating costs.

The oxygen driving force may be increased by increasing the saturated dissolved oxygen concentration C^* and reducing the dissolved oxygen concentration C_L .

25 Microorganism population growth is limited or prevented if the dissolved oxygen concentration C^* reaches too high a level. A concentration level above $4 \times 10^{-3} \text{ kg/m}^3$ has been found to be detrimental to *Sulfolobus*-like strains. Certain *Acidithiobacillus* strains, however, have been found to be tolerant to dissolved oxygen concentrations of up to $10 \times 10^{-3} \text{ kg/m}^3$.

The applicant has established that a lower limit for the dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. Thus, in order to provide an adequate, or optimum, supply of oxygen, the dissolved oxygen concentration in the sulphide mineral slurry must be monitored and, where appropriate, the addition of oxygen to the sulphide mineral slurry must be controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$.

On the other hand the dissolved oxygen concentration must not exceed an upper threshold value at which microorganism growth is prevented. It is pointed out that the upper threshold concentration depends on the genus and strain of microorganism used in the bioleaching process. A typical upper threshold value is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

As has been previously indicated the rate of sulphide mineral oxidation, which can be achieved when operating at a relatively low temperature of the order of from 40°C to 55°C , is limited. In order to increase the rate of oxidation it is desirable to make use of thermophiles and to operate at temperatures in excess of 60°C . Any suitable microorganism capable of operating within this temperature range may be used. The optimum operating temperature is dependent on the genus and type of microorganism used. Thus moderate thermophiles of the type *Sulfobacillus* are suitable for operating at a temperature of up to 65°C . Thermophiles of the type *Sulfolobus* are suitable for operating at temperatures of from 60°C to at least 85°C . *Sulfolobus metallicus*, for example, shows optimal growth in the temperature range of from 65°C to 70°C .

The applicant has established that the operation of the bioleaching process, using a gas enriched with oxygen, or pure oxygen, as the oxidant, at elevated temperatures of from 40°C to 85°C :

increases the specific sulphide oxidation duty of the reactor considerably;

results in an unexpected and significantly enhanced oxygen mass transfer rate;

increases the oxygen utilisation, providing that the dissolved oxygen concentration is controlled above the point where microorganism growth and mineral oxidation are prevented and below the point at which microorganism growth is inhibited; and

the overall power required for the oxidation of sulphide minerals is significantly reduced.

The method of the invention represents a significant improvement compared to a bioleach operation carried out at a temperature of from 40°C to 45°C with air.

5 The controlled addition of oxygen enriched air or pure oxygen directly into the bioreactor improves the oxygen utilisation efficiency. The oxygen utilisation for a conventional commercial bioleach plant (at least 100m³ in volume) operating at from 40°C to 45°C with air may be expected to achieve a maximum oxygen utilisation factor of from 40% to 50%. Consequently only 40% to 50% of the total mass of oxygen supplied to the bioleach plant is used to oxidise the sulphide minerals. With the method of the invention the oxygen utilisation is significantly higher, of the order of from 60% to 95%. The higher oxygen utilisation is achieved by
10 controlled oxygen addition and results from the enhanced oxygen mass transfer rate and by operating at low dissolved oxygen concentrations in the solution phase.

It will be appreciated that although high oxygen demand in bioleach reactors has come about primarily by the use of higher temperatures, rapidly leaching sulphide minerals at temperatures below 60°C, using mesophile
15 or moderate thermophile microorganisms, will have similarly high oxygen demands. The method of the invention is therefore not restricted to suit thermophiles or extreme thermophiles, but also mesophile and moderate thermophile microorganisms.

Another advantage of using air enriched with oxygen or pure oxygen is that the evaporation losses are
20 reduced, because there is less inert gas removing water vapour from the top of the reactor. This is particularly important in areas where water is scarce or expensive.

In carrying out the method of the invention the temperature of the slurry in the bioleach vessel or reactor may be controlled in any suitable way known in the art. In one example the bioleach reactor is insulated and
25 heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry is regulated using any suitable cooling system, for example an internal cooling system.

Table 1 shows typical data for specific sulphide oxidation duty and oxygen utilisation, when bioleaching with air at 40°C to 45°C, in two commercial bioreactors, Plant A and Plant B respectively, (greater than 100m³ in volume).

5 Table 1 Commercial Bioreactor Performance Results

Description	Units	Plant A	Plant B
Reactor temperature	°C	42	40
Reactor operating volume	m ³	471	896
Oxygen utilisation	%	37.9	43.6
Typical dissolved oxygen concentration	mg/l	2.5	2.7
Oxygen mass transfer coefficient	s ⁻¹	0.047	0.031
Specific oxygen demand	kg/m ³ /day	21.6	14.8
Specific sulphide oxidation duty	kg/m ³ /day	8.9	5.7
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.8

At low temperatures (40°C – 50°C), with air as the inlet gas, which applies to the results for the commercial reactors, Plant A and Plant B, presented in Table 1, the oxygen utilisations achieved are expected and the oxygen mass transfer coefficients (M) correspond to the applicant's design value. The applicant has determined that if the method of the invention were to be applied to Plant A, the plant performance would be significantly increased, as indicated by the results presented in Table 2.

Table 2 Predicted Improvement In Commercial Bioreactor Performance

	Units	Plant A - typical operation	Plant A - using the method of the invention
Reactor temperature	°C	42	77
Microbial type strain	-	<i>Acidithiobacillus</i>	<i>Sulfolobus</i>
Inlet gas oxygen content	% by volume	20.9	90.0
Oxygen utilisation	%	37.9	93.0
Typical dissolved oxygen concentration	mg/l	2.5	2.5
Specific oxygen demand	kg/m ³ /day	21.6	59.5
Specific sulphide oxidation duty	kg/m ³ /day	8.9	24.5
Specific power consumption per kg sulphide oxidised	kWh/kgS ²⁻	1.7	1.2

The results clearly show the benefit of the invention in achieving higher rates of reaction by the combination of bioleaching at high temperature, adding oxygen enriched gas and by controlling the dissolved oxygen concentration to a predetermined low level (e.g. 0.2×10^{-3} kg/m³ to 4.0×10^{-3} kg/m³). The specific sulphide oxidation duty of the reactor is increased by almost threefold. Clearly the upper dissolved oxygen concentration should not be increased above a value at which microorganism growth is inhibited or stopped.

Even though additional capital for the production of oxygen is required, the savings in reactor and other costs at least offset this additional expense. Additionally, the specific power consumption per kg sulphide oxidised is decreased by approximately one-third. In a plant oxidising 300 tonnes of sulphide per day, the power saving, assuming a power cost of US\$0.05 per kWh, would amount to US\$2.8 million per annum. The high oxygen utilisation and increased specific sulphide oxidation capacity of the reactor represent in combination a considerable improvement over conventional bioleaching practice conducted at lower temperatures, with oxygen supplied by air.

Bioleaching Plant

Figure 1 of the accompanying drawings illustrates a non-limiting example of the invention and shows a bioleaching plant 10 in which bioleaching is carried out, in accordance with the principles of the invention.

5

The plant 10 includes a bioreactor 12 with an agitator or mixer 14 which is driven by means of a motor and gearbox assembly 16.

10

In use a tank or vessel 18 of the reactor contains a sulphide mineral slurry 20. An impeller 22 of the agitator is immersed in the slurry and is used for mixing the slurry in a manner which is known in the art.

A probe 24 is immersed in the slurry and is used for measuring the dissolved oxygen concentration in the slurry. A second probe 26, inside the tank 18 above the surface level 28 of the slurry, is used for measuring the carbon dioxide content in the gas 30 above the slurry 20.

15

An oxygen source 32, a carbon dioxide source 34 and an air source 36 are connected through respective control valves 38, 40 and 42 to a sparging system 44, positioned in a lower zone inside the tank 18, immersed in the slurry 20.

20

The probe 24 is used to monitor the dissolved oxygen concentration in the sulphide mineral slurry 20 and provides a control signal to a control device 46. The control device controls the operation of the oxygen supply valve 38 in a manner which is known in the art but in accordance with the principles which are described herein in order to maintain a desired dissolved oxygen concentration in the slurry 20.

25

The probe 26 measures the carbon dioxide content in the gas above the sulphide mineral slurry 20. The probe 26 provides a control signal to a control device 48 which, in turn, controls the operation of the valve 40 in order to control the addition of carbon dioxide from the source 34 to a gas stream flowing to the sparger 44.

The air flow rate from the source 36 to the sparger 44 is controlled by means of the valve 42. Normally the valve is set to provide a more or less constant flow of air from the source 36 to the sparger and the additions of oxygen and carbon dioxide to the air stream are controlled by the valves 38 and 40 respectively. Although this is a preferred approach to adjusting the oxygen and carbon dioxide contents in the air flow to the sparger other techniques can be adopted. For example it is possible, although with a lower degree of preference, to adjust the air stream flow rate and to mix the adjustable air stream with a steady supply of oxygen and a variable supply of carbon dioxide, or vice versa. Another possibility is to have two separate air stream flows to which are added oxygen and carbon dioxide respectively. Irrespective of the technique which is adopted the objective remains the same, namely to control the additions of oxygen and carbon dioxide to the slurry

20.

Slurry 50 is fed from a slurry feed source 52 through a control valve 54 and through an inlet pipe 56 into the interior of the tank 18. The slurry feed rate may be maintained substantially constant, by appropriate adjustment of the valve 54, to ensure that slurry is supplied to the tank 18 at a rate which sustains an optimum leaching rate. The supplies of air, oxygen and carbon dioxide are then regulated, taking into account the substantially constant slurry feed rate, to achieve a desired dissolved oxygen concentration in the slurry 20 in the tank, and a desired carbon dioxide content in the gas 30 above the slurry. Although this is a preferred approach it is apparent that the slurry feed rate could be adjusted, in response to a signal from the probe 24, to achieve a desired dissolved oxygen concentration in the slurry. In other words the rate of oxygen addition to the slurry may be kept substantially constant and the slurry feed rate may be varied according to requirement.

Another variation which can be adopted is to move the probe 24 from a position at which it is immersed in the slurry to a position designated 24A at which it is located in the gas 30 above the level 28. The probe then measures the oxygen contained in the gas above the slurry i.e. the bioreactor off-gas. The oxygen content in the off-gas can also be used as a measure to control the dissolved oxygen concentration in the slurry, taking any other relevant factors into account.

Conversely it may be possible to move the carbon dioxide probe 26 (provided it is capable of measuring the dissolved carbon dioxide content) from a position at which it is directly exposed to the gas 30 to a position designated 26A at which it is immersed in the slurry in the tank. The signal produced by the probe at the position 26A is then used, via the control device 48, to control the addition of carbon dioxide from the source 34 to the air stream from the source 36.

Although the carbon dioxide source 34, which provides carbon dioxide in gas form, is readily controllable and represents a preferred way of introducing carbon into the slurry 20, it is possible to add suitable carbonate materials to the slurry 50 before feeding the slurry to the reactor. Carbonate material may also be added directly to the sulphide mineral slurry 20 in the reactor. In other cases though there may be sufficient carbonate in the sulphide mineral slurry so that it is not necessary to add carbon, in whatever form, to the slurry nor to control the carbon content in the slurry.

It is apparent from the foregoing description which relates to the general principles of the invention that the supply of oxygen to the slurry is monitored and controlled to provide a desired dissolved oxygen concentration level in the slurry 20. This can be done in a variety of ways e.g. by controlling one or more of the following in an appropriate manner namely: the slurry feed rate, the air flow rate from the source 36, the oxygen flow rate from the source 32, and any variation of the foregoing.

The carbon dioxide flow rate is changed in accordance with the total gas flow rate to the sparger 44 in order to maintain a concentration in the gas phase, i.e. in the gas stream to the reactor, of from 0.5% to 5% carbon dioxide by volume. This carbon dioxide range has been found to maintain an adequate dissolved carbon dioxide concentration in the slurry, a factor which is important in achieving effective leaching.

The addition of oxygen to the sulphide mineral slurry 20 is controlled in order to maintain the minimum dissolved oxygen concentration in solution at a value of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $4.0 \times 10^{-3} \text{ kg/m}^3$. The upper threshold value depends on the genus and strain of microorganism used in the bioleaching process and typically is in the range of from $4 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

Figure 1 illustrates the addition of oxygen from a source 32 of pure oxygen. The pure oxygen can be mixed with air from the source 36. Any other suitable gas can be used in place of the air. The addition of oxygen to air results to what is referred to in this specification as oxygen enriched gas i.e. a gas with an oxygen content in excess of 21% by volume. It is possible though to add oxygen substantially in pure form directly to the slurry. As used herein pure oxygen is intended to mean a gas stream which contains more than 85% oxygen by volume.

The temperature in the bioleach reactor or vessel may be controlled in any appropriate way using techniques which are known in the art. In one example the tank 18 is insulated and heating takes place by means of energy which is released by the oxidation of sulphides. The temperature of the slurry 20 is regulated using an internal cooling system 70 which includes a plurality of heat exchanger cooling coils 72 connected to an external heat exchanger 74.

The vessel 18 may be substantially sealed by means of a lid 80. Small vents 82 are provided to allow for the escape of off-gas. The off-gas may, if required, be captured or treated in any appropriate way before being released to atmosphere. Alternatively, according to requirement, the tank 18 may be open to atmosphere.

The microorganisms chosen for the leaching process will determine the leaching temperature, and vice versa. The applicant has found that a preferred operating temperature is above 60°C, for example in the range of 60°C to 85°C. In this range thermophilic microorganisms, in any appropriate combination, are employed. In the range of from 45°C to 60°C, on the other hand, moderate thermophiles are employed while at temperatures below 45°C mesophiles are used. These microorganisms may, for example, be chosen from those referred to hereinbefore.

Although the benefit of adding oxygen to the slurry which is to be leached, by making use of oxygen enriched air or, more preferably, by making use of substantially pure oxygen i.e. with an oxygen content in excess of 85%, is most pronounced at high temperatures at which greater leaching rates are possible, a benefit is nonetheless to be seen when oxygen enriched air or substantially pure oxygen is added to the slurry at lower temperatures, of the order of 40°C or even lower. At these temperatures the leaching rates are slower than

at elevated temperatures and although an improvement results from using oxygen enriched air the cost thereof is generally not warranted by the relatively small increase in leaching rate.

Test Results

5

10

The importance of maintaining an adequate supply of oxygen and hence a sufficiently high dissolved oxygen concentration to sustain microorganism growth and mineral oxidation is shown in the results presented in Figure 2. If the dissolved oxygen concentration is allowed to drop below 1.5 ppm, and particularly below 1.0 ppm, biooxidation becomes unstable, which is indicated by higher iron(II) concentrations in solution, of greater than 2 g/l. At consistent levels of biooxidation, achieved by maintaining a dissolved oxygen concentration above 1.5 ppm, in this experiment, iron(II) is rapidly oxidised to iron(III), and iron(II) concentrations remain generally below 1.0 g/l.

15

The results presented in Figure 2 were obtained from operation of a first or primary reactor of a continuous pilot plant treating a chalcopyrite concentrate at a feed solids concentration of 10% by mass and a temperature of 77°C, with *Sulfolobus*-like archaea.

20

The effect of increasing the oxygen content of the feed gas to a bioreactor and controlling the dissolved oxygen concentration, in accordance with the principles of the invention, was tested in an experiment using a 5m³ bioreactor which was operated with a continuous pyrite or blended pyrrhotite and pyrite flotation concentrate feed, at a temperature of about 77°C, using a mixed culture of *Sulfolobus*-like archaea and a solids density of 10% by mass. The carbon dioxide content in the bioleach inlet gas was controlled at a level of between 1 and 1.5 % by volume. The dissolved oxygen concentration was generally within the range 0.4 x 10⁻³ kg/m³ to 3.0 x 10⁻³ kg/m³. The results of the experiment are presented in Figure 3.

25

From the graphs presented in Figure 3 it is clear that, when sparging with air (enriched with carbon dioxide: 20.7% oxygen and 1.0% carbon dioxide), the maximum oxygen demand (directly proportional to the sulphide oxidation duty) was limited to 11.3 kg/m³/day, since the dissolved oxygen concentration which was achievable using air only (i.e. not enriched with oxygen) was just sufficient to maintain microorganism growth.

By controlling the oxygen content of the inlet gas, the oxygen addition rate, and the dissolved oxygen concentration in the slurry in the range of $0.4 \times 10^{-3} \text{ kg/m}^3$ to $3.0 \times 10^{-3} \text{ kg/m}^3$, the oxygen demand, i.e. the sulphide mineral oxidation rate, was increased dramatically. The dissolved oxygen concentration was controlled to a low value, but above the minimum limit for successful microorganism growth, so that the utilisation of oxygen was maximised. The results show the oxygen demand, or sulphide oxidation duty, was increased by over threefold. Thus by increasing the oxygen content in the inlet gas from 20.7% to a maximum of 90.8% the specific oxygen demand was increased from $11.3 \text{ kg/m}^3/\text{day}$ to $33.7 \text{ kg/m}^3/\text{day}$. In addition, by controlling the dissolved oxygen concentration to a low value, but above the minimum value for sustained microorganism growth, the oxygen utilisation was maximised. The oxygen utilisation showed a general increase with an increase in the oxygen content of the inlet gas from 29% (for an inlet gas oxygen content of 20.7%) to 91% (for inlet gas containing 85.5% oxygen).

The high oxygen utilisations achieved of well over 60% are much better than expected. Analysis of the results indicates that the oxygen mass transfer coefficient (M), as defined by equation (1), is significantly and unexpectedly enhanced for operation of the bioreactor at a high temperature (77°C) and with a high oxygen content in the inlet gas (from 29% to 91% in the experiment). In fact, the oxygen mass transfer coefficient (M) is increased by a factor of 2.69, on average, compared to the applicant's design value. This enhancement is after considering the improvement in the mass transfer coefficient due to temperature, which would be expected to increase the value of M by a factor of 1.59 for a temperature increase from 42°C to 77°C , according to the temperature correction factor proposed by Smith et al ⁽⁵⁾. This correction factor has been demonstrated experimentally to be valid for a temperature in the range of from 15°C to 70°C ⁽⁶⁾

The determination of the enhanced oxygen mass transfer coefficient is shown from the results presented in Figure 4, where the oxygen demand divided by the design oxygen mass transfer coefficient (M_{design}) is plotted against the oxygen driving force, as defined in equation (1). The slope of the regression line plotted through the data indicates the enhancement in the oxygen mass transfer coefficient by a factor of 2.69.

Process Example

The inventive principles in the preceding section have been described in the context of sulphide minerals in general and, as will be appreciated by those skilled in the art, these principles can be applied to nickel bearing sulphide minerals in particular.

Figure 5 of the accompanying drawings is a process flow chart illustrating the use of method of the invention for recovering nickel.

In Figure 5 the plant 10 which is shown in Figure 1 and which is described hereinbefore bears the same reference numeral. The oxygen and carbon dioxide sources bear the reference numerals 32 and 34 respectively. The nickel sulphide slurry is labelled with the numeral 50.

The slurry 50 is fed to the plant 10 which contains one or more bioleach reactors using oxygen enriched gas or pure oxygen, labelled 32, as the oxidant. The oxygen concentration in the reactor is controlled in the manner which has been described hereinbefore depending on the type of microorganism used.

The bioleaching process produces a bioleach residue slurry 100 which contains solubilised nickel, and iron predominantly in the ferric state.

Optionally at this point the bioleach residue slurry 100 may be subjected to a liquid/solid separation step 102 which produces waste 104 and solution 104 from which copper 108, a metal commonly associated with nickel, is recovered by solvent extraction and electrowinning 110. Raffinate 111 from the solvent extraction step is returned to the main process flow stream.

Referring again to the main process flow stream iron in the bioleach residue slurry is removed by precipitation 112 brought about by the addition of limestone 114. Optionally, if there is insufficient carbonate in the nickel concentrate 50, some of the carbon dioxide 116 generated in the iron precipitation may be introduced into the

slurry in the plant 10 in any appropriate way for example by being blended with the oxygen 32, by being added to the carbon dioxide source 34, or by being injected directly into the slurry.

Slurry 118 produced by the iron precipitation 112 is subjected to a liquid/solid separation step 120 to produce solids 122 which are disposed of and a solution 124 which is fed to a nickel solvent extraction step 126. Strip liquor 128 from the solvent extraction step 126 is obtained by stripping the loaded solvent with anolyte 130 from a nickel electrowinning step 132. The pH of the nickel solvent extraction loading stage is maintained using a suitable alkali 134.

10 Raffinate 136 produced during the solvent extraction step may be disposed of or recycled (138).

The impure nickel strip liquor 128 is sent to another solvent extraction step 140 where cobalt and other impurities are removed. The pH of the cobalt solvent extraction loading stage is maintained using a suitable alkali 142. Dilute sulphuric acid 144 is used to strip the organic solvent to produce an impure cobalt sulphate solution 146 for further purification.

The cobalt solvent extraction raffinate 148 forms an advance electrolyte for the nickel electrowinning stage 132 in which nickel cathodes 150 are produced.

20 Oxygen gas 152 generated at the anode during the electrowinning process 128 may be recycled to the source 32, or directly into the slurry in the plant 10, to supplement the oxygen requirements during the bioleaching process.

The method of the invention is not limited to the use of an electrowinning process for the recovery of nickel. Other techniques may be employed. For example pressure hydrogen reduction (PHR) may be used as the production method of nickel. As the PHR system is known in the art it is not further described herein. Its use is however indicated symbolically by means of a block 160 as an alternative to the electrowinning process 132. In the PHR process nitrogen gas is required for purging the nickel reduction autoclaves during the production cycle of nickel powder. If the oxygen source 32 is used on site then, as a by product, nitrogen gas

162 is generated. This gas may be used, as indicated, for purging the autoclaves used for nickel powder production in the PHR process.

As has been indicated it is possible to operate the bioleach plant 10 in parallel to a pressure acid leaching (PAL) system which is used for the recovery of nickel from lateritic ores. This option is illustrated by means of a block labelled 170 which represents a pressure acid leaching installation for the recovery of nickel from lateritic ores.

The volumes arising downstream of PAL processes are roughly an order of magnitude higher than the mass of nickel sulphide concentrates arising from sulphide nickel mines. Since the residue from the bioleach plant 10 is similar in nature to the residue from the PAL installation 170, i.e. each residue has a low pH, and contains solubilised nickel and iron, it is advantageous to treat the bioleach residue for nickel and cobalt recovery using the larger PAL downstream process equipment. Thus combining a nickel sulphide bioleach residue slurry (100) with a PAL residue slurry and treating the streams together thereafter brings about considerable economies of scale in terms of capital and operating costs.

Pilot Plant Test Work

Bioleach pilot plant test work was completed, using a predominantly pentlandite concentrate assaying 11.9% nickel, on a 0.849 m³ pilot plant consisting of 5 reactors configured as 1 primary reactor followed by 4 secondary reactors in series. The total primary volume was 237l and the total secondary volume was 612l. All test work was carried out at between 65°C to 68°C using a feed slurry containing 15% solids. The microorganism used was a mixed culture of *Sulfolobus*-like archaea. The oxygen utilisation results obtained in the primary stage during the test work, using analysis of inlet and outlet gas mixtures, are shown in Table 3.

Table 3 : Primary Reactor Nickel Dissolution and Oxygen Uptake Results for Thermophile Pilot Test Work

Retention Days	Ni Dissolution %	Specific S ²⁻ Oxidation Rate kg/m ³	Oxygen Consumption Rate kg/m ³ /h
2.0	83.5	0.729	1.58

The results in Table 3 may be compared to mesophile results obtained at 40°C to 45°C. This test work was completed using the same concentrate as before, containing 11.9% nickel. The primary reactor in this test work had a volume of 60l , and the feed contained 15.9% solids. The results are shown in Table 4.

Table 4 : Primary Reactor Nickel Dissolution and Oxygen Uptake Results for Mesophile Bioleaching

Retention Days	Ni Dissolution %	Specific S ²⁻ Oxidation Rate kg/m ³	Oxygen Consumption Rate kg/m ³ /h
2.4	68.3	0.534	1.16

These results indicate about a 40% increase in specific sulphide oxidation rate when using thermophiles according to the method of the invention.

REFERENCES

1. Bailey, A.D., and Hansford, G.S., (1996), Oxygen mass transfer limitation of batch bio-oxidation at high solids concentration. *Minerals Eng.*, 7(23), pp293-303.
2. Myerson, A.S., (1981), Oxygen mass transfer requirements during the growth of *Thiobacillus ferrooxidans* on iron pyrite, *Biotechnol, Bioeng.*, Vol 23, pp1413.
3. Peter Greenhalgh, and Ian Ritchie, (1999); Advancing Reactor Design For The Gold Bioleach Process; Minproc Ltd, Biomine 99, 23-25 Aug 1999, Perth Australia, pp52-60.
4. Brock Biology of Microorganisms, Eight Edition, 1997., Madigan M.T., Martinko J.M., Parker J., Prentia Hall International, Inc., London.
5. J.M. Smith, K van't Riet and J.C. Middleton, (1997), Scale-Up of Agitated Gas-Liquid Reactors for Mass Transfer, in Proceedings of the 2nd European Conference on Mixing, Cambridge, England, 30 March – 1 April 1997, pp.F4-51 – F4-66.
6. Boogerd, F. C., Bos, P., Kuenen, J. G., Heijnen, J. J. & Van der Lans, R. G. J. M, Oxygen and Carbon Dioxide Mass Transfer and the Aerobic, Autotrophic Cultivation of Moderate and Extreme Thermophiles : A Case Study Related to the Microbial Desulfurization of Coal, *Biotech. Bioeng.*, 35, 1990, p. 1111 – 1119.
7. Mayze, R. (1999) An Engineering Comparison of the Three Treatment Flowsheets in WA Nickel Laterite Projects; Alta 1999 Nickel/Cobalt Pressure Leaching and Hydrometallurgy Forum.

CLAIMS

1. A method of recovering nickel from a nickel bearing sulphide mineral slurry which includes the steps of:
 - 5 (a) subjecting the slurry to a bioleaching process,
 - (b) supplying a feed gas which contains in excess of 21% oxygen by volume, to the slurry, and
 - (c) recovering nickel from a bioleach residue of the bioleaching process
- 10 2. A method according to claim 1 wherein copper is removed from the bioleach residue before recovering nickel therefrom.
3. A method according to claim 2 wherein cobalt is removed from the bioleach residue before recovering nickel therefrom.
- 15 4. A method according to any one of claims 1 to 3 which includes the step of removing iron from the bioleach residue before recovering nickel therefrom.
5. A method according to claim 4 wherein the iron is precipitated from the bioleach residue by the addition of limestone to the residue.
- 20 6. A method according to claim 5 wherein carbon dioxide generated in the iron precipitation step is fed to the feed gas of step (b) or directly to the slurry.
7. A method according to any one of claims 1 to 6 wherein, in step (c), nickel is recovered using a solvent extraction and electrowinning process.
- 25 8. A method according to claim 7 wherein oxygen generated during the nickel electrowinning is fed to the feed gas of step (b) or directly to the slurry.

9. A method according to any one of claims 1 to 6 wherein, in step (c), nickel is recovered using a pressure hydrogen reduction process and nitrogen, produced during the generation of the feed gas supplied to the slurry in step (b), is used for purging autoclaves used for nickel powder production in the pressure hydrogen reduction process.

5

10. A method according to any one of claims 1 to 9 which is operated in parallel to a process for recovering nickel from lateritic ores by pressure acid leaching to produce a nickel laterite ore slurry and which includes the step of adding the bioleach residue to the nickel laterite residue slurry before carrying out step (c).

10

11. A method according to any one of claims 1 to 10 wherein the feed gas contains in excess of 85% oxygen by volume.

15

12. A method according to any one of claims 1 to 11 which includes the step of maintaining the dissolved oxygen concentration in the slurry within a desired range

13. A method according to claim 12 wherein the said dissolved oxygen concentration is maintained in the range of from $0.2 \times 10^{-3} \text{ kg/m}^3$ to $10 \times 10^{-3} \text{ kg/m}^3$.

20

14. A method according to any one of claims 1 to 13 which includes the step of controlling the carbon content of the slurry.

15. A method according to any one of claims 1 to 14 which includes the step of controlling the carbon dioxide content of the slurry in the range of from 0.5% to 5.0% by volume.

25

16. A method according to any one of claims 1 to 15 which includes the step of bioleaching the slurry at a temperature in excess of 40°C .

17. A method according to claim 16 wherein the said temperature is in the range of from 40°C to 100°C .

18. A method according to claim 17 wherein the said temperature is in the range of from 60°C to 85°C.
19. A method according to any one of claims 1 to 15 which includes the step of bioleaching the slurry at a temperature of up to 45°C using mesophile microorganisms.
- 5 20. A method according to claim 19 wherein the microorganisms are selected from the following genus groups: *Acidithiobacillus*; *Thiobacillus*; *Leptosprillum*; *Ferromicrobium*; and *Acidiphilium*.
- 10 21. A method according to claim 19 or 20 wherein the said microorganisms are selected from the following species: *Acidithiobacillus caldus* (*Thiobacillus caldus*); *Acidithiobacillus thiooxidans* (*Thiobacillus thiooxidans*); *Acidithiobacillus ferrooxidans* (*Thiobacillus ferrooxidans*); *Acidithiobacillus acidophilus* (*Thiobacillus acidophilus*); *Thiobacillus prosperus*; *Leptosprillum ferrooxidans*; *Ferromicrobium acidophilus*; and *Acidiphilium cryptum*.
- 15 22. A method according to any one of claims 1 to 15 which includes the step of bioleaching the slurry at a temperature of from 45°C to 60°C using moderate thermophile microorganisms.
- 20 23. A method according to claim 22 wherein the microorganisms are selected from the following genus groups: *Acidithiobacillus* (formerly *Thiobacillus*); *Acidimicrobium*; *Sulfobacillus*; *Ferroplasma* (*Ferriplasma*); and *Alicyclobacillus*.
- 25 24. A method according to claim 22 or 23 wherein the said microorganisms are selected from the following species: *Acidithiobacillus caldus* (formerly *Thiobacillus caldus*); *Acidimicrobium ferrooxidans*; *Sulfobacillus acidophilus*; *Sulfobacillus disulfidooxidans*; *Sulfobacillus thermosulfidooxidans*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; and *Alicyclobacillus acidocaldrius*.
- 25 25. A method according to any one of claims 1 to 15 which includes the step of bioleaching the slurry at a temperature of from 60°C to 85°C using thermophilic microorganisms.

26. A method according to claim 25 wherein the microorganisms are selected from the following genus groups: *Acidothermus*; *Sulfolobus*; *Metallosphaera*; *Acidianus*; *Ferroplasma* (*Ferriplasma*); *Thermoplasma*; and *Picrophilus*.
- 5 27. A method according to claim 25 or 26 wherein the said microorganisms are selected from the following species: *Sulfolobus metallicus*; *Sulfolobus acidocaldarius*; *Sulfolobus thermosulfidooxidans*; *Acidianus infernus*; *Metallosphaera sedula*; *Ferroplasma acidarmanus*; *Thermoplasma acidophilum*; *Thermoplasma volcanium*; and *Picrophilus oshimae*.
- 10 28. A method of recovering nickel from a slurry containing nickel bearing sulphide minerals which includes the steps of:
- (a) bioleaching the slurry using suitable bacteria at a temperature in excess of 40°C,
 - (b) controlling the dissolved oxygen concentration in the slurry within a predetermined range,
 - and
 - 15 (c) recovering nickel from a bioleach residue produced in step (a).
29. A method according to claim 28 wherein the said dissolved oxygen concentration is controlled by controlling the supply of oxygen to the slurry.
- 20 30. A method according to claim 29 wherein the oxygen is supplied to the slurry in the form of oxygen enriched gas or substantially pure oxygen.
31. A method according to any one of claims 28 to 30 wherein the said temperature is in the range of from 60°C to 85°C.
- 25 32. A method of enhancing the oxygen mass transfer coefficient from a gas phase to a liquid phase in a nickel bearing sulphide mineral slurry which includes the step of supplying a feed gas containing in excess of 21% oxygen by volume, to the slurry.

33. A method according to claim 32 wherein the feed gas contains in excess of 85% oxygen by volume.
34. A method according to claim 32 or 33 which includes the step of raising the temperature of the slurry.
- 5 35. A method of bioleaching an aqueous slurry containing nickel bearing sulphide minerals which includes the steps of:
- (a) bioleaching the slurry at a temperature above 40°C, and
 - (b) maintaining the dissolved oxygen concentration in the slurry in the range of from 0.2×10^{-3} kg/m³ to 10×10^{-3} kg/m³.
- 10 36. A method according to claim 35 wherein the dissolved oxygen concentration in the slurry is maintained by supplying gas containing in excess of 21% oxygen by volume to the slurry.
37. A method according to claim 35 or 36 wherein the temperature is in the range of from 60°C to 85°C.
- 15 38. A plant for recovering nickel from a nickel bearing sulphide mineral slurry which includes a reactor vessel, a source which feeds a nickel bearing sulphide mineral slurry to the vessel, an oxygen source, a device which measures the dissolved oxygen concentration in the slurry in the vessel, a control mechanism whereby, in response to the said measured dissolved oxygen concentration, the
- 20 supply of oxygen from the oxygen source to the slurry is controlled to achieve a dissolved oxygen concentration in the slurry within a predetermined range, and a recovery system which recovers nickel from a bioleach residue from the reactor vessel:
39. A plant according to claim 38 which includes an installation for recovering nickel from lateritic ores by
- 25 pressure acid leaching to produce a nickel laterite residue slurry which is combined with the said bioleach residue from the reactor vessel, and the combined slurry and residue are fed to the said recovery system.

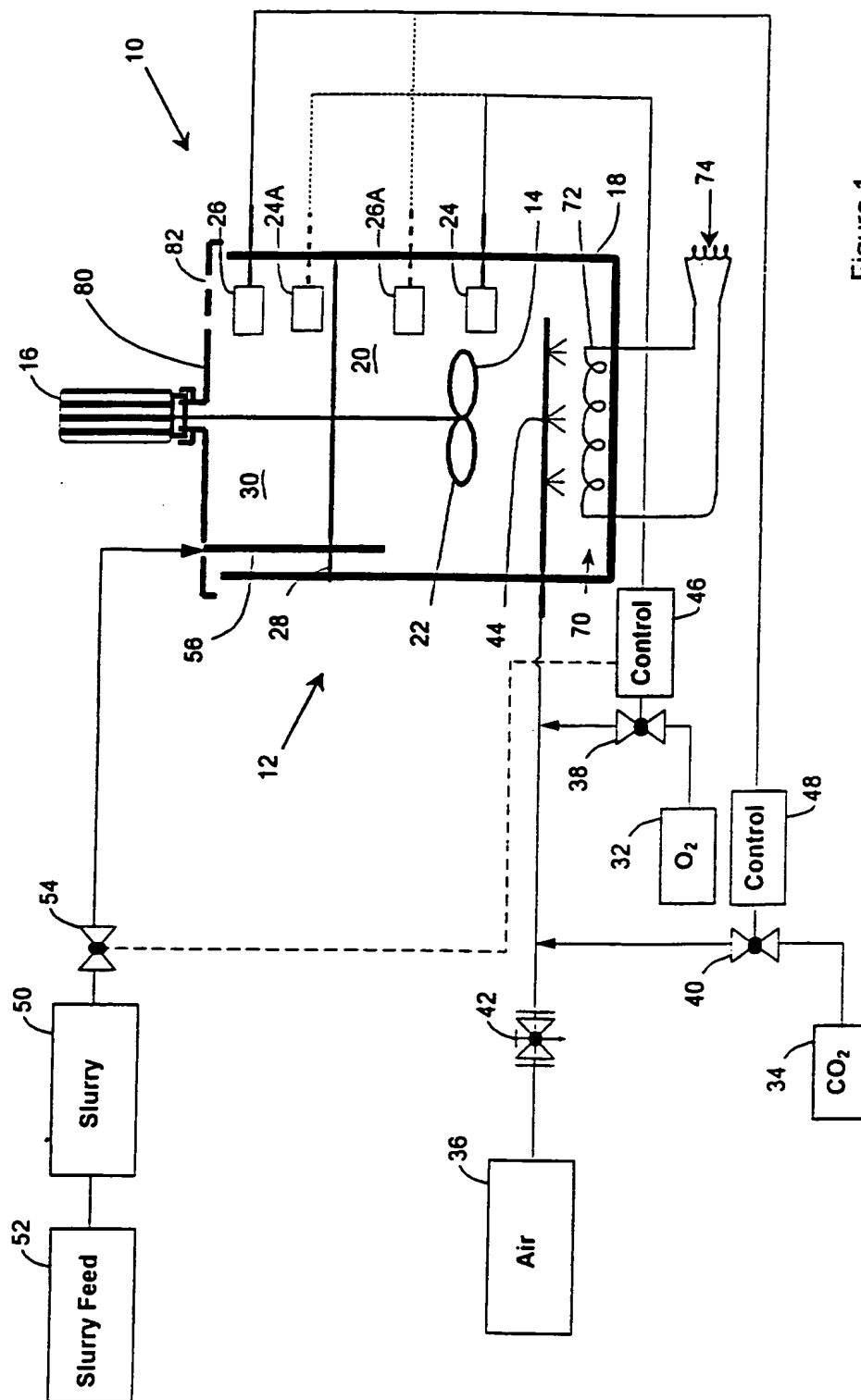


Figure 1

Ferrous Concentration vs. Dissolved Oxygen Concentration

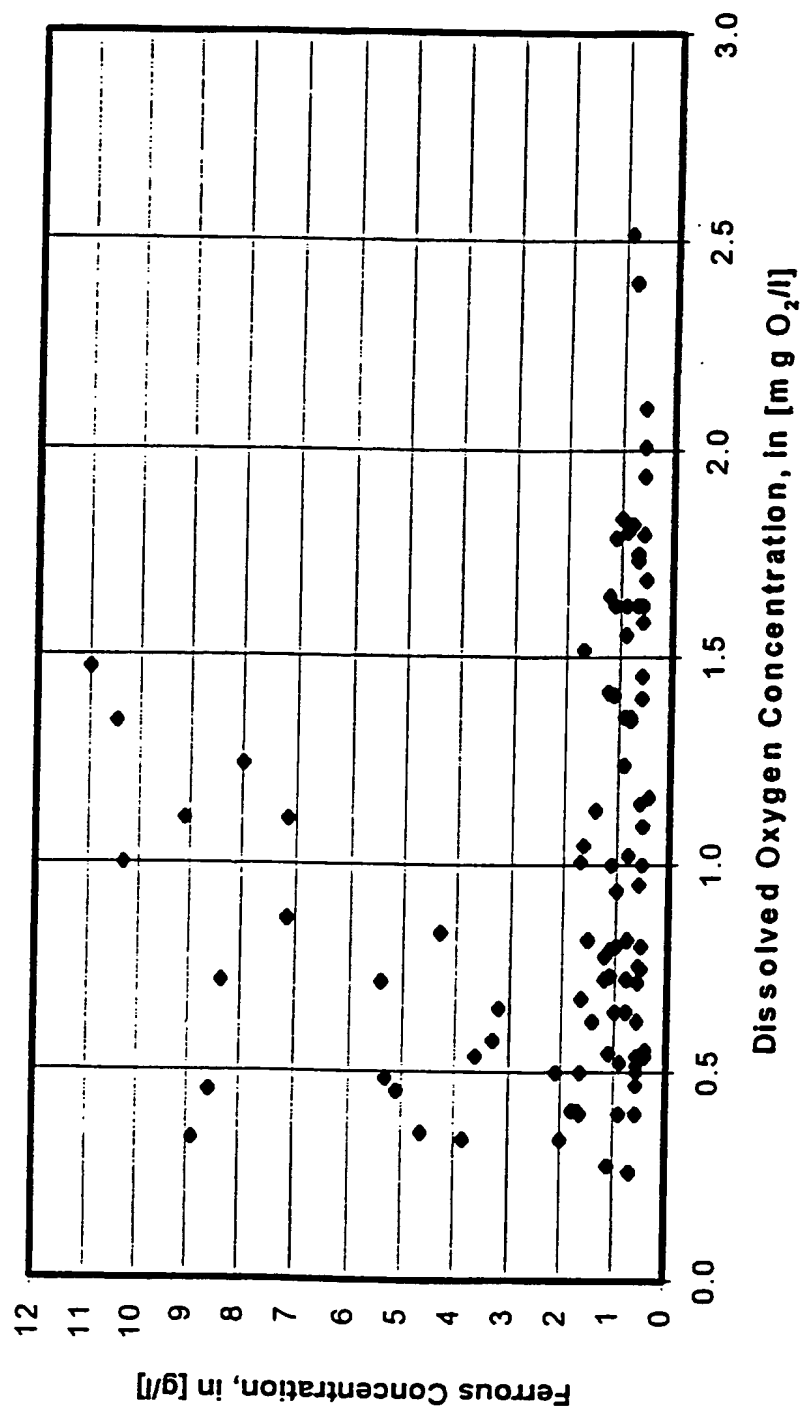


Figure 2 Results Showing The Effect of Reduced Microbial Oxidation On Iron(II) Concentration Levels In Solution As A Result Of Operating At Low Dissolved Oxygen Concentrations

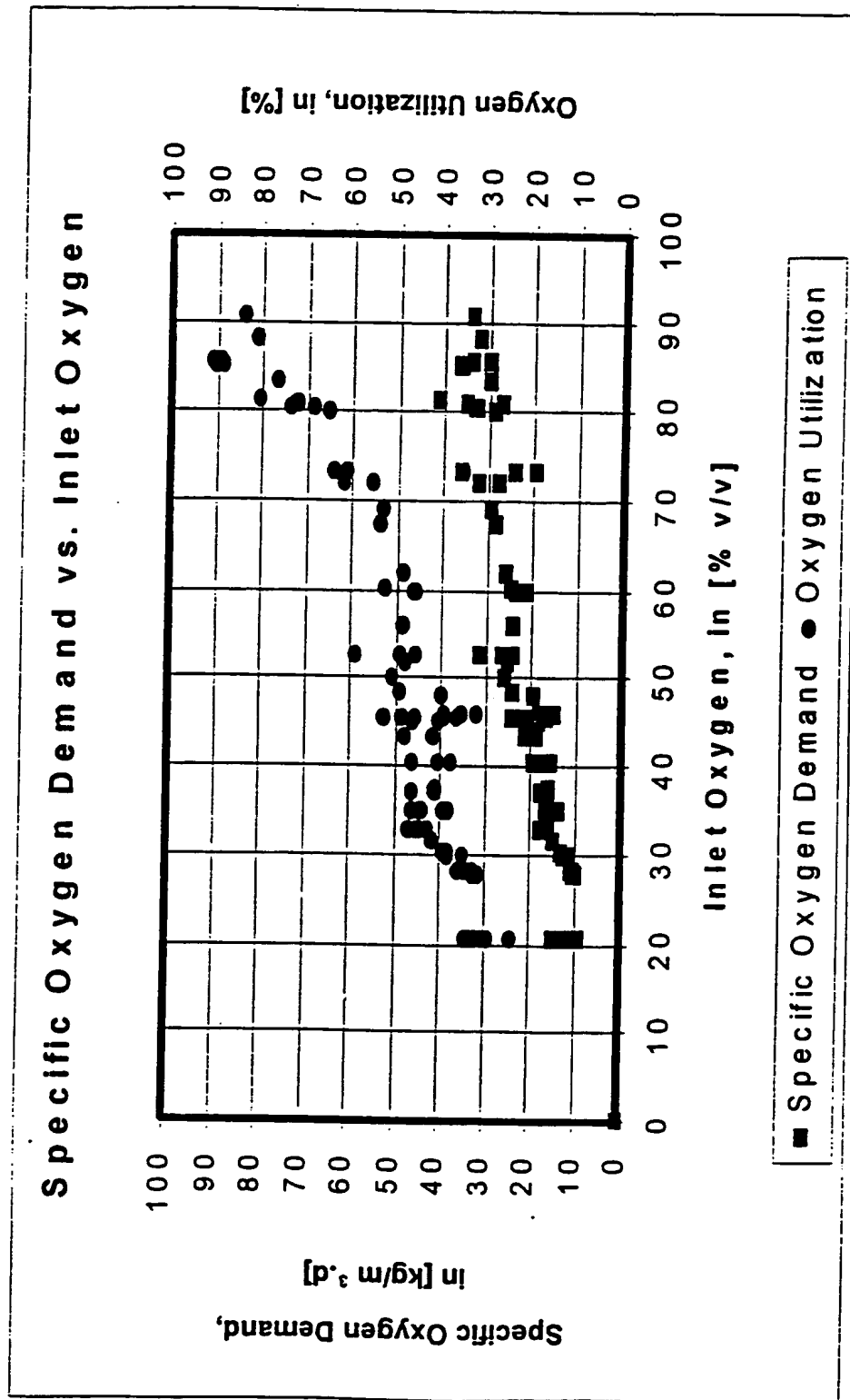


Figure 3 Results Showing The Increase In Specific Oxygen Demand and Oxygen Utilisation Achieved By Increasing The Oxygen Content Of The Inlet Gas Under Controlled Conditions By The Method Of The Invention

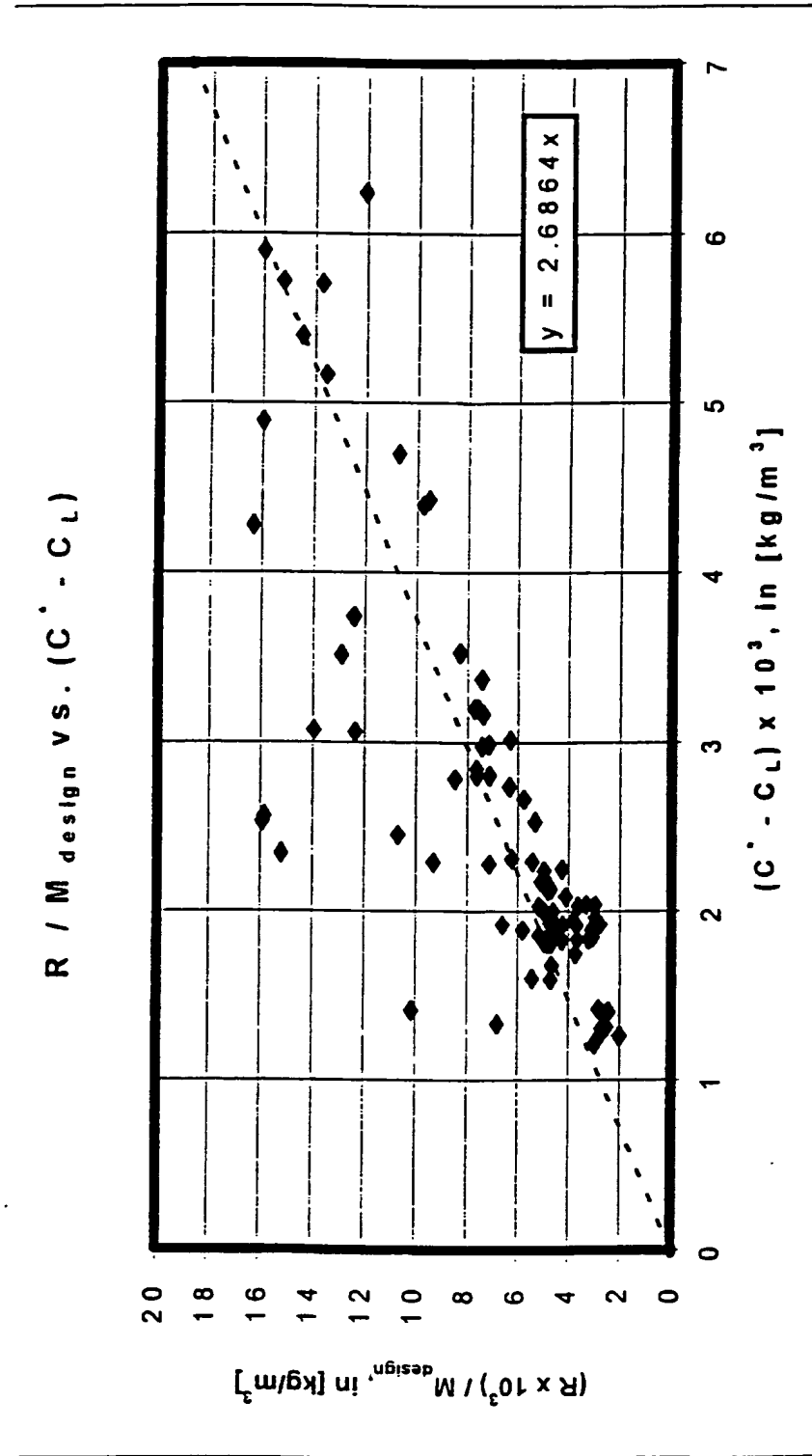
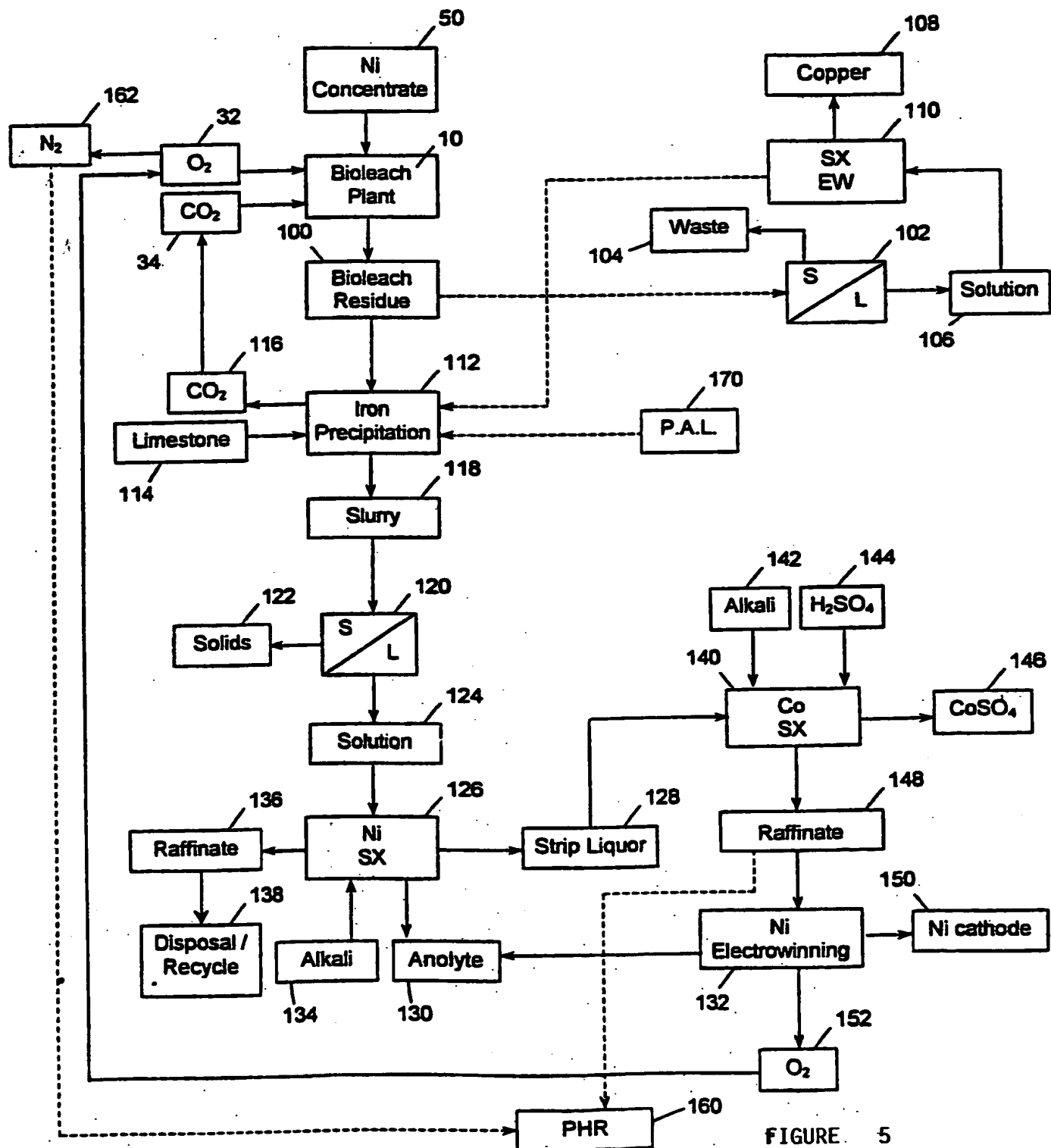


Figure 4 Results Demonstrating The Enhancement Of The Oxygen Mass Transfer Coefficient



INTERNATIONAL SEARCH REPORT

International Application No.

PCT/ZA 00/00162

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C22B3/18 C22B23/00 B22F9/26

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C22B B22F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAJ, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 225 256 A (TOLMIN MINERAL TECHNOLOGIES NV) 30 May 1990 (1990-05-30) page 1, line 15 -page 2, line 13; claims 1,3-6,8-13,20-23; figures 1-8 page 6, line 19 -page 7, line 20	1-5,7, 10-39
Y	US 5 007 620 A (EMMETT JR ROBERT C ET AL) 16 April 1991 (1991-04-16) column 15, line 49 - line 65; figures 1-7,20,21,33 column 19, line 3 - line 12 column 21, line 45 - line 53	1-5,7, 10-39
Y	WO 98 26100 A (BHP MINERALS INT INC) 18 June 1998 (1998-06-18) example 2	1-5,7, 10-37

-/--



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *Z* document member of the same patent family

Date of the actual completion of the international search

4 December 2000

Date of mailing of the international search report

12/12/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040. Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Bombeke, M

INTERNATIONAL SEARCH REPORT

Intern: al Application No

PCT/ZA 00/00162

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2 291 870 A (GENCOR LTD) 7 February 1996 (1996-02-07) page 4 -page 6 ---	1,4,5,7, 19-21
Y	WO 99 09226 A (JONES DAVID L ;COMINCO ENG SERVICES (CA)) 25 February 1999 (1999-02-25) figures 2-4 ---	2-5,7, 10,39
Y	EP 0 808 910 A (UNIV MICHIGAN TECH) 26 November 1997 (1997-11-26) column 8, line 3 - line 25; figure 1 ---	38
P,X	WO 00 29629 A (MILLER PAUL CHARLES ;RHODES MIKE (AU); WINBY RICHARD (AU); BACTECH) 25 May 2000 (2000-05-25) page 3, line 14 -page 4, line 26 -----	1,11, 16-34

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2225256 A	30-05-1990	AU 630889 B	12-11-1992
		AU 4262989 A	12-04-1990
		US 5021069 A	04-06-1991
		ZA 8907627 A	25-09-1991
US 5007620 A	16-04-1991	US 4974816 A	04-12-1990
		US 4732608 A	22-03-1988
		AT 78240 T	15-08-1992
		AU 607901 B	21-03-1991
		AU 6858087 A	13-08-1987
		CA 1329989 A	07-06-1994
		DE 3780452 A	20-08-1992
		DE 3780452 D	20-08-1992
		DE 3780452 T	11-03-1993
		EP 0294387 A	14-12-1988
		ES 2001827 A	16-06-1988
		FI 883604 A	01-08-1988
		GR 870202 A	05-06-1987
		JP 63502796 T	20-10-1988
		NZ 219219 A	26-04-1990
		WO 8704694 A	13-08-1987
		US 5057284 A	15-10-1991
		US 5227136 A	13-07-1993
		ZW 15687 A	28-10-1987
		BR 8700558 A	08-12-1987
		US 4968008 A	06-11-1990
		US 4728082 A	01-03-1988
		ZA 8606691 A	24-06-1987
		ZA 8700817 A	28-10-1987
		ZM 1587 A	28-03-1988
		ZW 11686 A	18-02-1987
WO 9826100 A	18-06-1998	US 5626648 A	06-05-1997
		AU 720713 B	08-06-2000
		AU 1288697 A	03-07-1998
		BR 9612802 A	28-03-2000
		EP 0948655 A	13-10-1999
GB 2291870 A	07-02-1996	AU 689598 B	02-04-1998
		AU 2726295 A	15-02-1996
		CA 2155051 A	02-02-1996
		FI 953487 A	02-02-1996
		ZA 9506204 A	12-03-1996
WO 9909226 A	25-02-1999	AU 8796398 A	08-03-1999
		AU 8847598 A	08-03-1999
		BR 9811945 A	22-08-2000
		WO 9909225 A	25-02-1999
		CN 1267338 T	20-09-2000
		CN 1271392 T	25-10-2000
		EP 1012351 A	28-06-2000
		EP 1012352 A	28-06-2000
		NO 20000727 A	21-03-2000
EP 0808910 A	26-11-1997	US 5827701 A	27-10-1998
		AU 725634 B	19-10-2000
		AU 2141197 A	27-11-1997
		CA 2205151 A	21-11-1997

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/ZA 00/00162

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0808910 A		JP 10113694 A	06-05-1998
		US 6043022 A	28-03-2000
		ZA 9704368 A	24-08-1998
WO 0029629 A	25-05-2000	AU 1141400 A	05-06-2000